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THE VAPOR PRESSURE AND HEATS OF VAPORIZATION OF NICKEL

AIR FORCE MATERIALS LABORATORY

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$\sigma_{50}(\text{Ag}) = 4.48 \times 10^{-16} \text{ cm}^2$; $\sigma_{60}(\text{Ag}) = 4.50 \times 10^{-16} \text{ cm}^2$; the maximum cross section for O atom at 87.8 volts: $\sigma_{m88(\text{O})} = 1.56 \times 10^{-16} \text{ cm}^2$; the maximum (total cross section) for O_2 at 123 volts: $(\sigma_{m123})_t(\text{O}_2) = 2.80 \times 10^{-16} \text{ cm}^2$. The maximum cross section for nickel at approximately 70 volts is: $\sigma_{m70}(\text{Ni}) = 4.19 \times 10^{-16} \text{ cm}^2$ while the cross section at 60 volts is: $\sigma_{60}(\text{Ni}) = 4.10 \times 10^{-16} \text{ cm}^2$.

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Nickel Oxide						
Heat of Vaporization						
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Langmuir Vaporization of Solids						

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GERARD L. HAURY

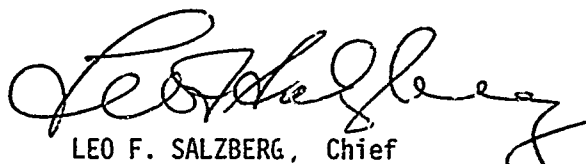
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FOREWORD

This report was prepared under Project 7360, "The Chemistry and Physics of Materials," Task 736001, "High Temperature Physics". The work was performed intermittently during the period September 1970 to September 1972 by Dr. Emile Rutner, and Mr. G. L. Haury. Mr. Michael Bodeker assisted in the experimental work, while Mr. Gerard L. Haury was the Project Engineer.

This technical report has been reviewed and is approved.



LEO F. SALZBERG, Chief
Electromagnetic Materials Division
AF Materials Laboratory

ABSTRACT

A determination was made of the vapor pressure and heat of vaporization of solid nickel between 1233 and 1658°K. The value of the second law heat of vaporization which was obtained was: $(\Delta H_0^\circ)_v = 115.8 \pm 5.5$ kcal/mole, while the value of the third law heat was: $(\Delta H_0^\circ)_v = 102.6 \pm 2.1$ kcal/mole. A statistical treatment of all the available data of the vapor pressure of nickel gave the following "best value" for the heat of vaporization of solid nickel: $(\Delta H_0^\circ)_{vs} = 101.45 \pm 0.62$ kcal/mole. The best vapor pressure equation of solid nickel between 1250°K and 1710°K which was obtained was: $\ln P_s(\text{mm}) = 23.50 \pm 0.35 - \frac{50,600 \pm 301}{T}$, while the vapor pressure equation for liquid nickel between 1816 and 1895°K was: $\ln P_l(\text{mm}) = 21.98 \pm 0.05 - \frac{47,775 \pm 210}{T}$. Corrected estimates of the heats of dissociation of the molecules (Ni_2) and (NiO) were also obtained and were: $D_0^\circ(\text{Ni}_2) = 61.7 \pm 0.6$ kcal/mole; and $D_0^\circ(\text{NiO}) = 92.7 \pm 0.9$ kcal/mole (millimeter equals Torr).

Best values of the absolute ionization cross sections to be used in mass spectrometry for Ag, O, O_2 , and Ni were deduced from the literature. The maximum cross section for silver at 72 volts: $\sigma_{m72}(\text{Ag}) = 4.63 \times 10^{-16} \text{ cm}^2$; while $\sigma_{50}(\text{Ag}) = 4.48 \times 10^{-16} \text{ cm}^2$; $\sigma_{60}(\text{Ag}) = 4.50 \times 10^{-16} \text{ cm}^2$; the maximum cross section for O atom at 87.8 volts: $\sigma_{m88(\text{O})} = 1.56 \times 10^{-16} \text{ cm}^2$; the maximum (total cross section) for O_2 at 123 volts: $(\sigma_{m123})_t(\text{O}_2) = 2.80 \times 10^{-16} \text{ cm}^2$. The maximum cross section for nickel at approximately 70 volts is: $\sigma_{m70}(\text{Ni}) = 4.19 \times 10^{-16} \text{ cm}^2$ while the cross section at 60 volts is: $\sigma_{60}(\text{Ni}) = 4.10 \times 10^{-16} \text{ cm}^2$.

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INTRODUCTION

Since there is a continuous need for information on the thermodynamics, chemical kinetics, and the physical behavior of materials at high temperatures, studies of the mass loss rates and kinetics of phase transformations, including the kinetics of vaporization of some selected materials have been undertaken. To increase our capability to carry out these studies the temperature range of the experimental techniques which were used in previous mass loss studies has been extended. The system, which was constructed to determine mass loss rates, was characterized by establishing the operating power levels of the induction furnace, and calibrating the techniques for measuring temperatures; and also by determining the reproducibility and errors of mass loss measurements. The material chosen for the characterization studies was nickel.

Upon examination of available information on the heats of vaporization and the vapor pressure of nickel, it became apparent that a need existed for a determination of the best value for these quantities; therefore, a statistical evaluation of the information in the literature was undertaken. A recalculation of the values of the vapor pressures obtained by the mass spectrometric technique was also performed due to availability of more recent data on ionization cross sections and thermodynamic functions.

The report is divided into sections describing the experimental technique used in this work, and the resulting measured vapor pressure and temperature relation of nickel; the statistical evaluation of the data available in the literature on the vapor pressures of nickel and heats of vaporization of nickel; the reestimation of the heats of vaporization of nickel oxide; reestimation of the heats of dissociation of the NiO and Ni_2 molecules and a determination of the best available values for the ionization cross sections of silver and nickel atoms.

Throughout this report mm and Torr are used interchangeably.

PART I

EXPERIMENTAL PROCEDURES

A. Description of the Apparatus

To determine vapor pressures of materials at high temperatures it is desirable to make continuous weighings of the samples without exposing them intermittently to the atmosphere since exposure to the atmosphere often results in absorption of gases which cause errors in the determination of the mass loss rates. The errors from this source were reduced by the use of a recording electrobalance, coupled with an induction furnace, and heating the sample in vacuo. A sample thus heated can be continuously or intermittently weighed. To utilize the apparatus properly, observations were made on the temperature uniformity of the heated sample, on the variations of the recorded weight of the sample with the power level of the furnace, and on the sensitivity of the microbalance. The system was tested by using it to measure the vapor pressure of nickel by determining the mass loss rates of a cylinder of nickel.

The apparatus consisted of a 6 in i.d. x 11 in pyrex bell jar (a) Figure 1 (photographs, Figures 2 and 3) which housed the RF induction coil (b) and specimen (c), which was mounted directly over the diffusion pump (h) to afford maximum pumping speed from the specimen chamber. The coil (b) consisted of five turns of 1/4-inch copper refrigeration tubing and was 2-1/4 inches i.d. x 1-3/4 inches in length. The specimen (c) was suspended and centered in the inside of the coil (b) by means of a 0.005 inch diameter tungsten wire looped around the specimen so as to form a harness; the two ends were hooked to an inconel wire three inches above the specimen, and the inconel wire, in turn, was hooked to a nylon thread hanging from the end of the balance beam at (d). The electrobalance (e) (a Cahn type RH) was enclosed in a glass vacuum bottle (f). The balance was coupled to the bell jar and pumping system via a short length of vacuum hose (g) which afforded a flexible connection. The hose was raised to allow insertion or removal of the specimen from the system. The entire system was evacuated to 10^{-5} mm pressure by means of a 6-inch oil diffusion pump (h) and a Welch

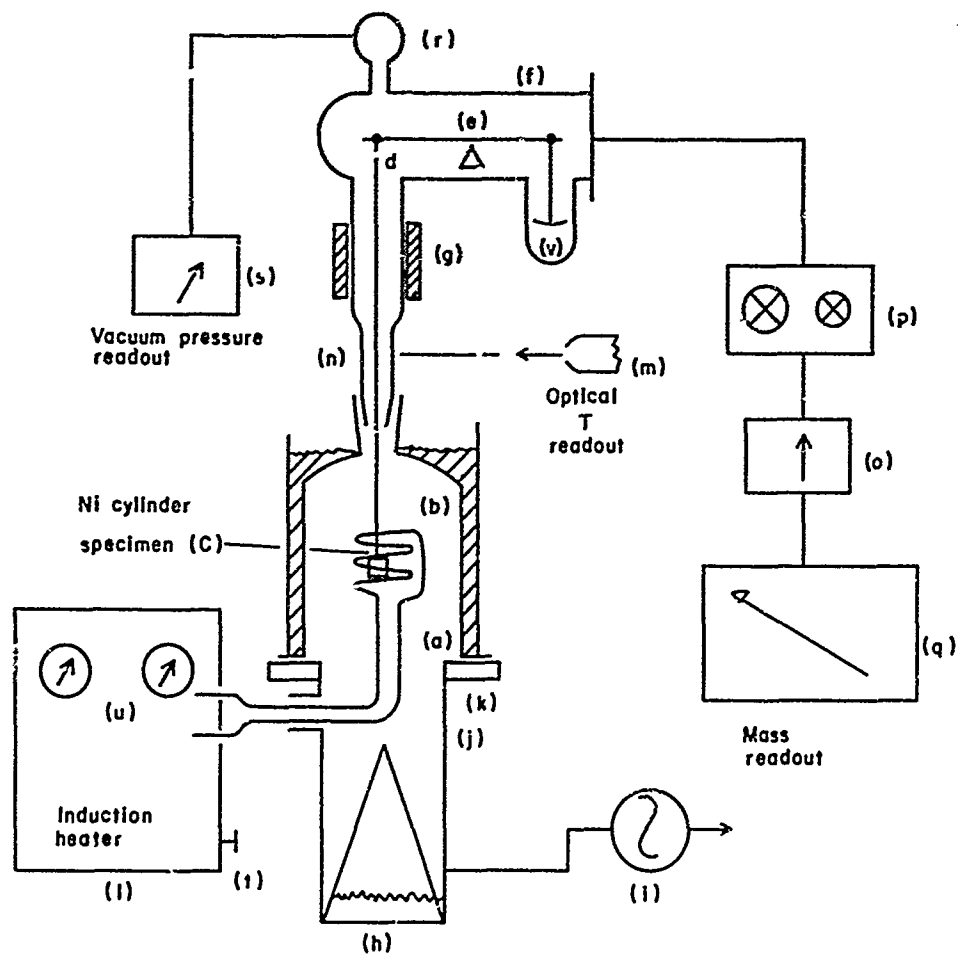


Figure 1. Experimental Apparatus for Measuring Weight Losses

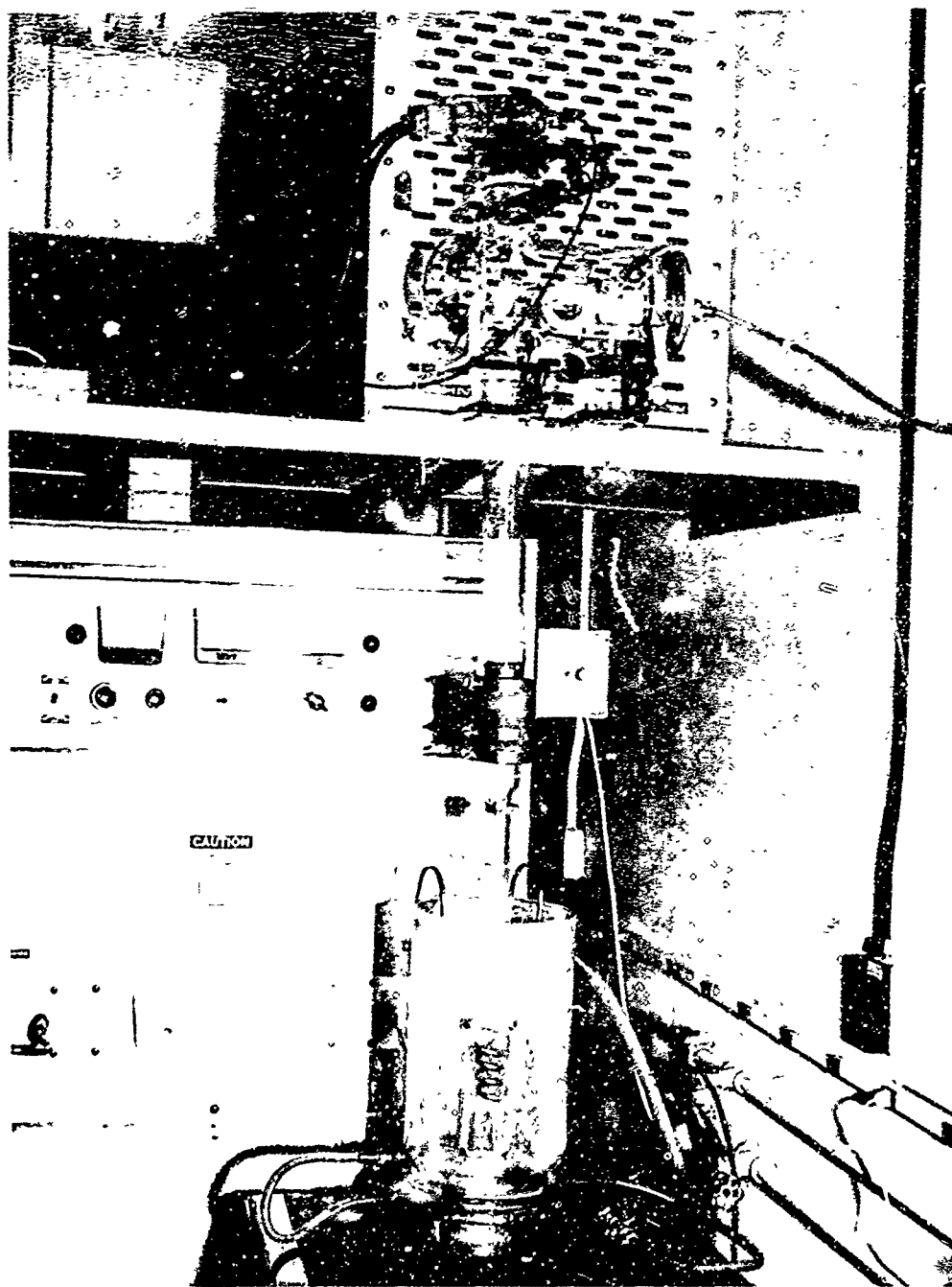


Figure 2. Heating Coil and Micro Balance as Noted in Figure 1

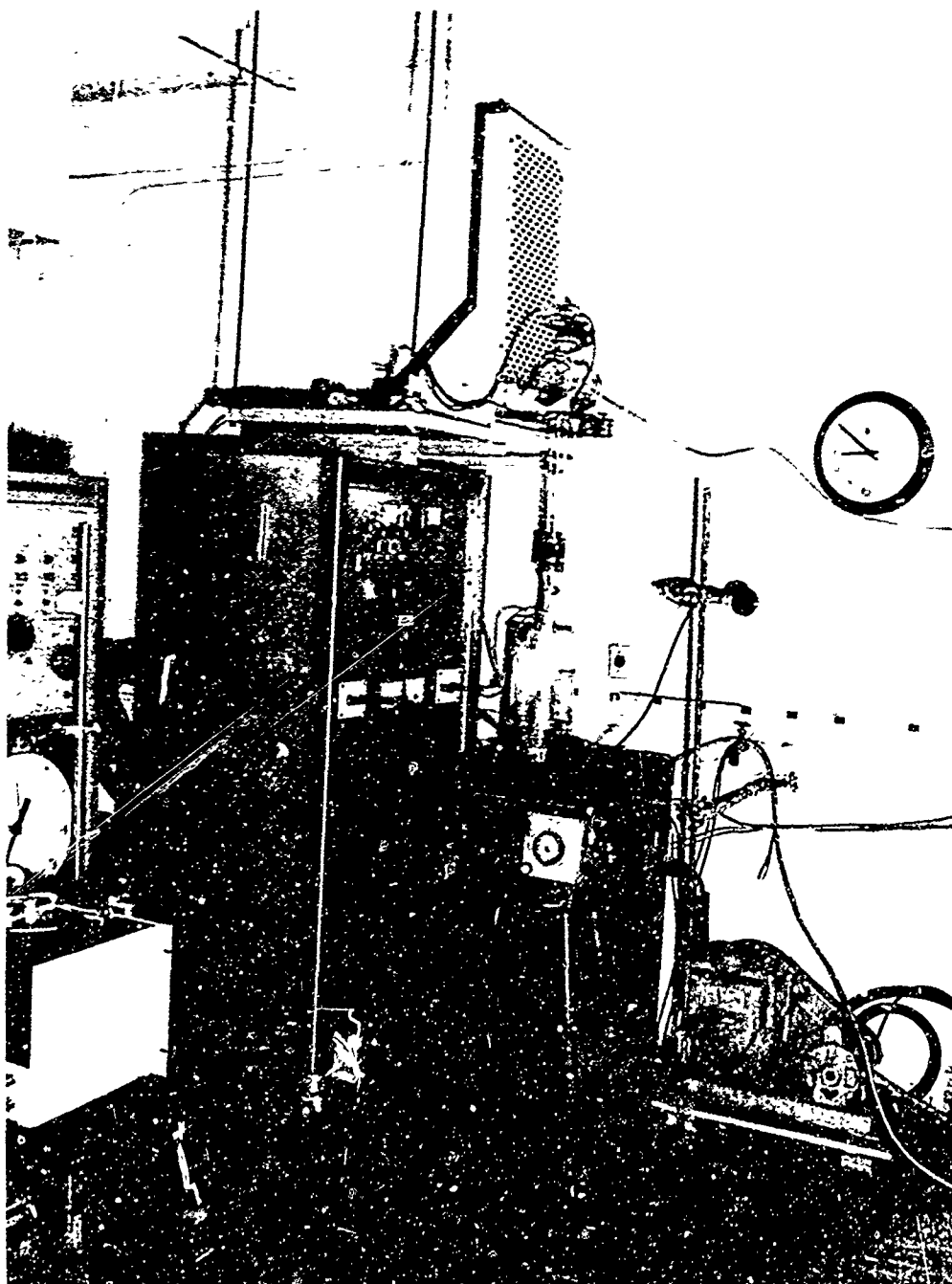


Figure 3. Furnace, Micro Balance, Pyrometer as Noted in Figure 1

Model 1397 Duo Seal mechanical vacuum pump (i). Baffles were inserted as shown at (j) in order to reduce the back diffusion of the pump oil into the specimen chamber. The brass flange (k) was hollow and water was pumped through it for cooling. The outside of the bell jar (a) was surrounded by a water jacket through which was circulated distilled water to cool the specimen chamber surfaces and thus remove condensable gases. The cooling water was circulated in a closed system to avoid corrosion of the equipment, and the formation of deposits on the bell jar surfaces. The induction furnace (l) and RF coil (b) were cooled by the same system. A Leeds and Northrup disappearing filament type optical pyrometer (m) was used to read specimen temperatures via the mirror (n).

The induction furnace (l) was a Sealomatic Electronics Corp. Model 2000-20KW which was operated at 3 megahertz.

The electrobalance (e) was monitored by means of a Hewlett Packard Model 419A D.C. null voltmeter (o). The voltmeter received its input from the balance control box (p). The output of the voltmeter (o) was fed to a Brown (Model 153) single point recorder (q) when continuous weight change determinations were performed. The pressure of the system was determined by means of an ionization gauge (r). The gauge (r) and pressure control-monitor box (s) were Veeco Vacuum Gauge type RG 31x. The power input to the specimen was manually adjusted at furnace control knob (t). Power input and stability were monitored at the oscillator tube plate current and voltage meters. The electrobalance was mounted on a 3/4-inch thick plywood platform contained in an aluminum framework. One end of the framework was anchored to a concrete sidewall of the building while the other end was suspended from a concrete ceiling by means of two 1/2-inch steel tie rods (see photograph Figure 3). The mounting minimized vibrations and isolated the balance from the induction furnace.

B. Experimental Procedure

(1) Calibration of Pyrometer with NBS STD lamp (IPTS 1948)

The optical pyrometer was calibrated against a standard ribbon filament strip lamp at several temperatures between 900 and 1600°C. The temperatures read on the pyrometer during calibration were found to be within $\pm 5^\circ\text{C}$ of the standard lamp certification curve. The pyrometer was also "calibrated" by placing the standard lamp in "situ" of the sample; thus correcting for radiation losses due to absorption and length of path between sample and pyrometer. These calibrations were carried out by placing the standard lamp at position (b) (Figures 1 and 4) and focusing the pyrometer on the image of the lamp in mirror (n). The pyrometer was positioned at (m). Two observers made sets of three temperature readings each on the pyrometer for each fixed power level of the lamp, resulting in six temperature readings for each calibration point. The two sets of readings at any given temperature were found to agree to $\pm 5^\circ\text{C}$. The calibration curve of "true" vs. "read" temperature consisted of six different points thus determined.

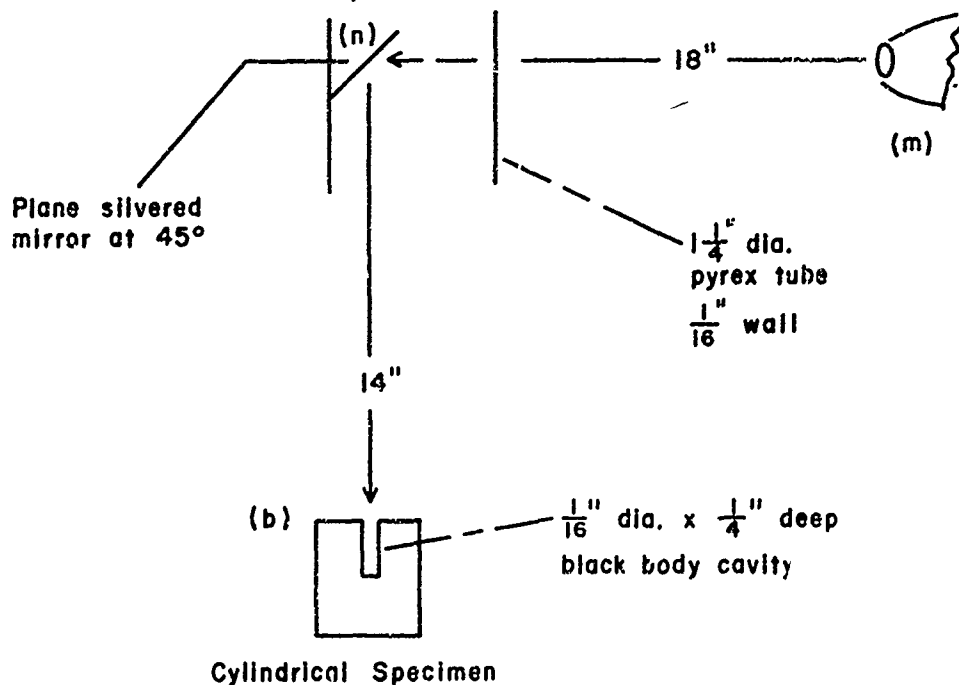


Figure 4. Arrangement of Optical Pyrometer for Temperature Measurements

(2) Weighings

The masses of the samples were determined by reading the mass dial of the microbalance control box (p) when voltmeter (c) indicated zero voltage. Each division on the mass dial corresponded to 0.5 milligram and the dial could be read to two-tenths of one division giving a sensitivity of 0.1 milligram. The reproducibility of individual weighings, however, was found to be ± 0.3 milligram, on the basis of thirteen individual weighings of a specimen under experimental conditions. The electrical noise level was low, and no appreciable fluctuations of the meter (c) were observed when the mass dial was read. The electrobalance was checked prior to each experiment by the addition and subtraction of milligram calibration weights to the balance tare weight. The weight as read out on the mass dial at (p) agreed with the calibration weight to ± 0.1 milligram.

(3) Specimen

The nickel specimen was machined from a one-half-inch diameter nickel rod of 99.95%+ purity which was obtained from Galland Schlesinger Chemical Company, Carle Place, New York. A black body cavity 1/16 inch in diameter by 1/4-inch deep was drilled in the center of one end of the specimen such that it could be sighted for the optical temperature measurement (see Figure 4). The specimen was cleaned with benzene to remove any oil or other impurities which might be absorbed on the surface, and the cylinder was suspended as described in Section A. The required counterweights were added to pan (v) so that the total weight loss could be read out at (p) without breaking the vacuum. Next, the specimen was centered as well as possible in coil (b) and the system evacuated to 10^{-5} Torr and power applied from induction heater (1) by adjusting the control (t) to the desired power level. The sample was outgassed by heating to approximately 1400°C for 15 minutes prior to each run. The power output as observed at the meters (u) was constant to $\pm 4\%$ at all temperatures throughout the runs. After the sample reached the desired temperature the sample weight was observed at the recorder (q), until a constant weight loss rate was observed indicating that the sample was at a constant temperature and had been adequately degassed. The initial

time of a run was taken as the time at which the mass loss rate became constant.

When the power was turned on, the nickel specimen experienced a solenoid force which was due to the field in the induction coil. This force varied with the power setting, but was constant at a given power setting as is indicated by the agreement in weight loss rates as determined from the total weight loss measurements divided by the time and that determined from the recorder chart slope of weight vs time measurements. The agreement was within 12% when nine terminations were compared. The solenoid force was of the order of one milligram at the average power setting of about 0.3 kilowatt.

The sample was heated at a given temperature long enough so that the resulting weight loss was several milligrams. Thus keeping the probable weighing error to less than 1% without causing an appreciable change in the sample surface area, the sample area was between 5 and 6 cm². The weight of the specimen was recorded immediately before and after each heating period at a given temperature with the heater power turned off; thus a total weight loss at each temperature was obtained.

Weight losses were also determined from a continuous weighing of the sample as a function of time when the power settings were 0.7 kw or less at a frequency of 2.8 Megahertz. At power settings higher than 0.7 kw the noise level was too high to give a consistent weight with the power on and, therefore, the only weight determinations which were made were those obtained with the power shut off.

For a given determination of the heat of vaporization, mass loss rates were measured at six to ten temperatures spaced at equal intervals. To obtain adequate mass losses at low temperatures, runs lasting several hours were necessary, whereas, at the high temperatures, runs of twenty minutes gave adequate mass losses. All runs were at least twenty minutes long in order to make the error in the time determination insignificant, and to minimize the error in mass loss determinations which occur during the time period that the sample is being heated and cooled.

C. Treatment of Data

If the rate of mass loss per unit area from a freely evaporating solid is equal to the vaporization rate of the solid in equilibrium with its vapor, then rate of mass loss per unit area (\dot{m}_i) due to a given gaseous species (i) at the temperature (T) is related to the standard heat of vaporization [ΔH_{vi}°] for the species (i) by Equation 1 (Reference 1).

$$\frac{d(\ln \dot{m}_i)}{d(1/T)} = \frac{d(\ln P_i)}{d(1/T)} + \frac{T}{2} = \frac{\Delta H_{vi}^\circ}{R} + \frac{T}{2} \quad (1)$$

In Equation 1, P_i is the equilibrium vapor pressure of the ith species.

The slope of a plot of $\ln \dot{m}_i$ vs. $1/T$, is proportional to the heat of vaporization if we assume that the difference in the heat capacity of the gas and solid is zero. The error due to the differences in the heat capacity is minimized if we assume that ΔH_v° is taken at the mean temperature of the determination.

In considering the vaporization of nickel, the gaseous species is assumed to be only nickel atoms; (References 2, 4). Therefore, the vapor pressure can be calculated by using the following relation:

$$\dot{m} = \frac{P}{17.14} \sqrt{\frac{M}{T}} \quad (2)$$

if $\dot{m} = \text{g} \times \text{cm}^{-2} \times \text{sec}^{-1}$

P = pressure in millimeters

M = molecular weight gm/mol

T = degrees kelvin for nickel, $M = 58.71$ g/mol

$$\text{and } P = \frac{\dot{m} \sqrt{T}}{0.447}$$

A computer program was written to obtain a least square fit to a linear function of $\ln m$ vs. $1/T$. The data used in the program was the observed time, the mass loss, and the temperature. The slope $[d \ln m/d (1/T)]$, Figure 5, is related to $[\Delta H_v^\circ]$ by Equation 1 above. The value of $[\Delta H_v^\circ]$ thus obtained was referred to \bar{T} , the temperature obtained by averaging the inverse temperatures of the set of observations of the mass loss vs. time, and is designated in the literature as the 2nd law heat of vaporization. The series of values for the second law heat of vaporization, $[\Delta H_v^\circ]_{\bar{T}}$, thus obtained were corrected to the reference states at the reference temperature $[T_r]$ of 298°K and 0°K by the use of Equation 3 below. (Reference 3).

$$\left[\frac{H^\circ - H^\circ}{T} \right]_{\bar{T}} - \left[\frac{H^\circ - H^\circ}{T} \right]_{T_r} + [\Delta H_v^\circ]_{\bar{T}} = [\Delta H_v^\circ]_{T_r} \quad (3)$$

The best values of ΔH_0° and ΔH_{298}° which were obtained are shown in Table II and Figure 5.

Third law values of $[\Delta H_v^\circ]_{T_r}$ were obtained utilizing free energy functions as given in the standard thermodynamic tables (Reference 3). For example values of $-\frac{(G^\circ - H_{298}^\circ)}{T}$ for the gas and solid were used as shown below, in Equation 5 to obtain the $[\Delta H_v^\circ]$ for the vaporization of the solid nickel, Reaction 4,



$$\left[\frac{G^\circ - H_{298}^\circ}{T} \right]_v + \left[\frac{G^\circ - H_{298}^\circ}{T} \right]_s + R \ln P = \left[\frac{\Delta H_v^\circ}{T} \right]_{298} \quad (5)$$

Table II gives the data used to obtain values of the third law heat of vaporization.

An estimate was made of the probable errors in each of the determinations of the vapor pressures on a basis of the probable errors in the measurements (mass loss, and temperature, Table I). The estimated error in the weighing was ± 0.3 milligram thus the % error varies with the total mass loss (Δm Table IV) at a given point. This error was compared with that determined from a least squares computer program which determined the error in the slope of the line, $\ln P$ vs. $1/T$, as shown in Figure 5. The error in the slope can be compared to those calculated on the basis of the probable errors in T and Δm , by comparing the errors in the pressure obtained by the equations given in Table IV. Comparison of errors was made using the data in Table II. The results are given in Table IV.

The data reported on the vapor pressures of nickel and heats of vaporization of nickel as determined by the second and third law methods were combined with other data in the literature to determine the best values for the vapor pressures and heats of vaporization. Part II, Sec. 1 (B(1)), of this report discusses the statistical methods for combining data from various laboratories to obtain the best values.

TABLE I

MASS LOSS RATES FOR LANGMUIR VAPORIZATION OF NICKEL

Run No.	T°K	Δt min.	Δm mg	\dot{m} g/cm ² /sec x 10 ⁶	Pressure Torr x 10 ⁶
3a,b,c	1233	126	0.1	0.0033	0.2598
4b,c	1658	8	50.6	27.00	2443.
4	1563	10	11.6	4.03	356.7
4	1393	102	2.0	0.73	6.083
6d	1558	29	22.3	2.143	189.2
6	1447	59	9.5	0.4487	38.18
6	1513	26	31.6	3.388	294.8
6	1277	248	0.45	0.0051	0.4078
6	1345	169	0.55	0.0091	0.7465
6	1428	117	1.05	0.0253	2.139
6	1546	43	10.9	0.7148	62.89
6	1648	11	26.7	6.846	621.8
6	1562	34	16.8	1.393	123.2
6	1610	21	37.0	4.700	421.8
10e	1458	142	5.3	0.118	10.08
10	1488	85	6.3	0.235	20.28
10	1523	44	6.8	0.490	42.80
10	1563	30	9.2	0.970	85.79
10	1593	18	17.7	3.11	277.6
10	1613	12	14.5	3.82	343.1
10	1613	20	22.3	3.53	317.0
11e	1403	339	2.5	0.0237	1.986
11	1373	394	1.7	0.0139	0.5150
11	1363	274	0.9	0.0106	0.8760
12e	1353	215	0.3	0.0045	0.3310
12a,b	1483	48	4.5	0.302	26.00
12a,b	1543	15	4.8	1.03	90.51
12	1433	59	0.5	0.027	2.270

a These points eliminated from 2nd law determination.

b These points eliminated from 3rd law determination.

c Specimen surface area = 4.05 cm².

d New specimen same stock as c. Area = 5.91 cm².

e New specimen same stock as c. Area = 5.17 cm².

TABLE II
THIRD LAW VALUES $(\Delta H_0^\circ)_v$ FOR THE VAPORIZATION OF NICKEL

T°K	Pressure atmospheres x 10 ⁹	ΔH_{298}° kcal/mol
1345	0.982	102.92
1428	2.810	106.16
1546	82.70	97.75 ^a
1447	50.20	99.25
1558	249.0	101.72
1562	162.0	103.33
1563	469.0	100.06
1610	555.0	102.46
1648	818.0	104.17
1658	3210.0	99.65
1363	1.153	103.86
1353	0.435	105.74
1433	2.990	106.37
1483	34.20	102.83
1543	119.1	102.46
1523	56.30	104.00
1488	26.70	103.86
1458	13.30	103.84
1613	417.0	103.57
1613	451.0	103.34
1593	526.0	102.74
1563	112.5	104.50
1403	2.620	105.17
1373	0.6780	106.03
1393	2.004	100.72 ^b
1233	0.3413	97.09 ^{ab}
1277	0.5366	99.36 ^b
1513	387.9	97.53 ^{ab}

a. Points not used to determine 3rd law value.

b. Points not used to determine 2nd law value.

3rd law $\Delta H_0^\circ = 102.6 \pm 2.1$ kcal/mole.

3rd law $\Delta H_{298}^\circ = 103.1 \pm 2.1$ kcal/mole.

2nd law $\Delta H_0^\circ = 115.8 \pm 5.5$ kcal/mole.

2nd law $\Delta H_{298}^\circ = 116.3 \pm 5.5$ kcal/mole.

TABLE III
FREE ENERGY FUNCTIONS FOR NICKEL SOLID AND NICKEL GAS (a)

T°K	$[-(G^\circ - H^\circ_{st})/T]_s$ cal/°K/mole	$[-(G^\circ - H^\circ_{st})/T]_g$ cal/°K/mole
1345	47.74	12.43
1428	48.02	12.80
1546	48.38	13.56
1447	48.08	12.88
1558	48.43	13.35
1562	48.44	13.36
1563	48.44	13.37
1610	48.58	13.56
1648	48.69	13.71
1658	48.72	13.75
1363	47.81	12.51
1353	47.78	12.46
1433	48.04	12.81
1483	48.20	13.02
1543	48.38	13.56
1523	48.32	13.20
1488	48.21	13.06
1458	48.12	12.93
1613	48.59	13.57
1613	48.59	13.57
1593	48.53	13.49
1563	48.44	13.37
1403	47.94	12.24
1373	47.84	12.56
1393	47.91	12.65
1233	47.48	11.92
1277	47.51	12.12
1513	48.29	13.16

*st - standard state at 298°K.

a. Tabulated values interpolated from Hultgreen, Reference 3.

TABLE IV

ESTIMATED EXPERIMENTAL ERRORS IN THE OBSERVED VAPOR PRESSURES OF NICKEL,
AND DEVIATIONS BETWEEN OBSERVED AND CALCULATED PRESSURES

T°K	Observed P(Torr) x 10 ⁶	% Error Predicted in P (a)	Calculated P(Torr) x 10 ⁶ b	% dev. (c)
1345	0.7465	33.6	0.1493	+400.0
1353	0.3310	100.0	0.7580	+56.3
1363	0.8760	33.0	0.4380	+100.0
1373	0.5150	17.7	1.772	-70.9
1403	1.990	12.0	2.388	-16.7
1428	2.139	29.5	11.29	-81.1
1433	2.270	60.0	14.44	-84.3
1447	38.18	3.4	5.83	+555.0
1458	10.10	5.7	10.04	+0.6
1483	26.00	6.7	13.47	+93.0
1488	20.30	4.8	25.17	-19.4
1523	42.80	4.4	73.19	-30.4
1543	90.50	6.3	85.38	+6.0
1546	62.88	3.0	161.4	-61.0
1558	189.2	1.5	74.2	+155.0
1562	123.2	0.7	158.9	-22.5
1563	85.80	3.3	272.8	-68.6
1563	356.7	1.9	42.7	+735.4
1593	278.0	1.7	289.1	-3.8
1610	421.8	1.0	404.4	+4.3
1613	343.0	2.1	617.4	-44.4
1613	317.0	1.4	684.7	-53.7
1648	621.8	1.3	1623.	-61.7
1658	2442.	0.8	442	+453.0

(a) Predicted errors on the basis of expected errors in the measurement of P.

$$\% \text{ error} = \left[\frac{0.3}{\Delta m} + \frac{2.5}{T} \right] \times 100$$

(b) Calculated on basis of least squares fit as shown in Figure 5.

(c) % deviation from least squares line.

$$\left[\frac{\text{observed P} - \text{calculated P}}{\text{calculated P}} \right] \times 100$$

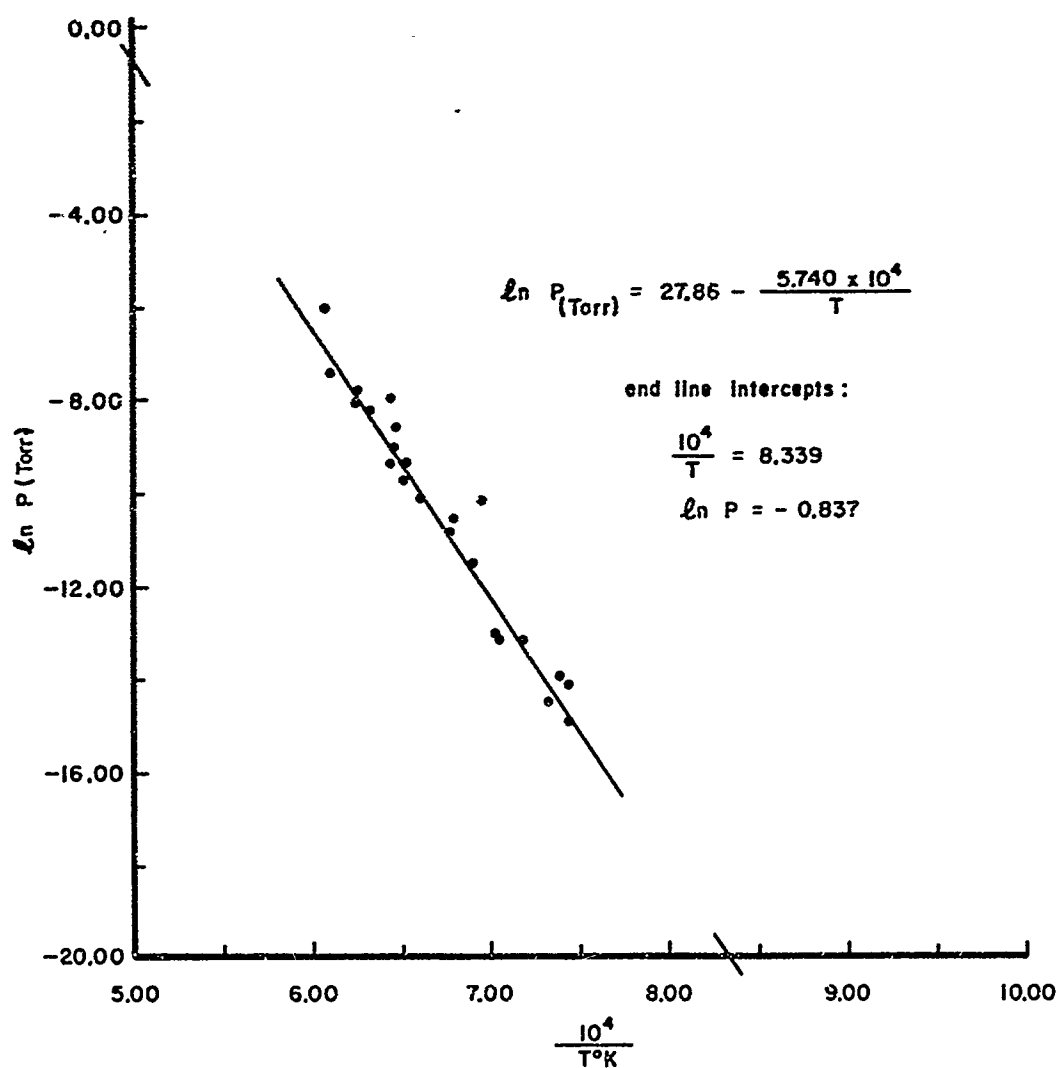


Figure 5. Second Law Plot for the Determination of $(\Delta H^\circ_0)_v$ of Nickel (solid). (a) Points with deviations $>2\sigma$ (r.m.s) deviation eliminated.

PART II -

EVALUATION OF THERMODYNAMIC DATA ON THE VAPORIZATION
NICKEL AND NICKEL OXIDE

SECTION I Examination of the Available Data on the Vapor Pressures and
Heats of Vaporization of Nickel

An opportunity to determine the best value of the heat of vaporization of nickel and to obtain an expression for the vapor pressure was offered by the available data in the literature. The variety of techniques reported for the determination of the vapor pressure of nickel all reduce to a determination of the mass loss rate from a sample as a function of temperature, with the exception of the determination by Grimley et al (Reference 4). All the data can be reduced in terms of the second and third laws of thermodynamics as discussed under "Treatment Data", Part I, Section 1C of this report.

In determining the suitability of data for use in determining the best value, certain criteria were applied for evaluating the experimental techniques and also an examination was made of the internal and external consistencies of the data.

The following discussions cover each reported set of experiments and also the opinions of the validity of some of the data as expressed by other evaluators. The sources of data are given in the references and in Table V.

A. Evaluation of Experimental Techniques

In the evaluation of the experimental techniques we took note of (1) methods of temperature measurement, (2) condition of samples, (3) method of weight loss determination, (4) consistencies between second and third law values of heats of vaporization, (5) external consistencies of heats of vaporization.

a. Haury, this report, Part I, determined the temperatures of his samples by sighting on a black body hole in the sample with a calibrated pyrometer. The complete experimental calibration of the

TABLE V
REPORTED VAPOR PRESSURES OF NICKEL USED IN DETERMINING
BEST VALUES OF ΔH_0° BY SECOND AND THIRD LAW METHODS

Temperature °K	Pressure Torr	Temperature °K	Pressure Torr	Temperature °K	Pressure Torr
Haury, Table I		Johnston & Marshall, Reference (8)		Langmuir & McKay, Reference (10) ^g	
1393 ^{c,d}	0.6083×10^{-5}	1583	0.3520×10^{-6}	1318	0.2436×10^{-5}
1345 ^d	0.7465×10^{-6}	1308	0.4260×10^{-6}	1409	0.5072×10^{-4}
1610	0.4218×10^{-3}	1307	0.4560×10^{-6}	1532	0.3301×10^{-3}
1546	0.5288×10^{-4}	1397	0.5500×10^{-5}	1544	0.3850×10^{-3}
1447	0.3818×10^{-4}	1397 ^a	0.6200×10^{-5}	1604 ^d	0.1271×10^{-2}
1563	0.3567×10^{-3}	1387	0.4330×10^{-5}	Nesmeynov & Teh Tik-Mang, References (5), (6) ^e	
1558	0.1892×10^{-3}	1415	0.8280×10^{-5}	1525	0.1170
1562	0.1232×10^{-3}	1465	0.2830×10^{-4}	1483	0.4620×10^{-1}
1658	0.2443×10^{-2}	1507	0.7540×10^{-4}	1478	0.4690×10^{-1}
1648	0.6218×10^{-3}	157 ^f	0.3440×10^{-3}	1443	0.2330×10^{-1}
1277 ^c	0.4078×10^{-8}	1778	0.3460×10^{-3}	1439	0.2040×10^{-1}
1428	0.2139×10^{-5}	1397 ^c	0.6200×10^{-5}	1401	0.9800×10^{-2}
1403	0.1990×10^{-5}	1466 ^c	0.3290×10^{-4}	1411	0.1060×10^{-1}
1373	0.5150×10^{-6}	Grimley, Burns & Ingraham, Reference (4) ^b		1365	0.3680×10^{-2}
1363	0.8760×10^{-6}	1575 ^c	0.2060×10^{-3}	1320 ^d	0.1640×10^{-2}
1433	0.2270×10^{-5}	1596 ^c	0.3400×10^{-3}	1550 ^d	0.1730
1523	0.4280×10^{-4}	1606	0.4130×10^{-3}	1371 ^c	0.3540
1488	0.2030×10^{-4}	1624	0.6460×10^{-3}	Morris, Zellars, Payne & Kipp, Reference (11) ^f	
1458	0.1010×10^{-4}	1625	0.6460×10^{-3}	1895	0.3870×10^{-1}
1513	0.3170×10^{-3}	1630	0.7170×10^{-3}	1894	0.3860×10^{-1}
1613	0.3430×10^{-3}	1646	0.1060×10^{-2}	1885	0.3320×10^{-1}
1593	0.2780×10^{-3}	1651	0.1160×10^{-2}	1816	0.1280×10^{-1}
1563	0.8580×10^{-4}	1657	0.1280×10^{-2}	1876	0.3060×10^{-1}
1543	0.9050×10^{-4}	1659	0.1300×10^{-2}	1868	0.2640×10^{-1}
1353	0.3310×10^{-6}	1673	0.1660×10^{-2}	1853	0.2210×10^{-1}
1483	0.2600×10^{-4}	1679	0.1910×10^{-2}	1848	0.2020×10^{-1}
1233 ^{c,d}	0.2598×10^{-6}	1684	0.2130×10^{-2}	1842	0.1910×10^{-1}
1513 ^{c,d}	0.2948×10^{-3}	1679	0.1930×10^{-2}	1839	0.1780×10^{-1}
Bryce, Reference (12) ^a		1684	0.2140×10^{-2}	1836	0.1750×10^{-1}
1273	0.2450×10^{-6}	1707	0.3130×10^{-2}	1828	0.1510×10^{-1}
1252	0.9800×10^{-7}	1709 ^d	0.3280×10^{-3}	1848	0.2040×10^{-1}
1423	0.1400×10^{-4}	1587 ^d	0.3360×10^{-3}	1860	0.2430×10^{-1}
1391	0.3690×10^{-5}			1821	0.1360×10^{-1}
1341	0.1100×10^{-5}			1862 ^d	0.2560×10^{-1}
1324	0.1050×10^{-5}				
1299	0.7510×10^{-6}				

Data points were omitted whose deviations were greater than 2σ (r.m.s. deviation) from second law and third law best values.

- a.. All points reported included.
- b. This data has been corrected for errors in cross sections. See p. 22.
- c. Eliminated from second law individual determination.
- d. Eliminated from third law individual determination.
- e. Not used in final composite determination. See p. 20.
- f. Liquid phase vaporization corrected for heat of fusion. See p. 21, 26.
Not used to determine best value of A by second or third law.
- g. Not used in composite third law determinations.

pyrometer which is described on page 7 included corrections for the absorption of radiation by the sample viewing windows. Although observations of the "brightness" temperature on the external surface of the cylinder were made, no data was recorded on the extent of the variation of the temperature on the surface. The weight loss rate was obtained by continuous weighing with a microbalance.

The lack of consistency between the second and third law values of the heat of vaporization which is shown in Table II, arises from the fact that the second law values are subject to larger errors than third law values, as indicated by the error analysis in Part I, Section 1C.

b. The data of Nesmeyanov and Tik-Mang (References 5, 6, and 7) were evaluated but not utilized because the vapor pressures which were determined by measuring the weight loss rate from a Knudsen cell were 10^3 times larger than those previously and subsequently reported.

c. Johnston and Marshall (Reference 6) determined the vapor pressure of nickel by a free vaporization or Langmuir technique. They determined the temperature by sighting on a blackbody hole in the sample which was doughnut shaped. They made brightness intensity corrections for the absorption of radiation by the windows. The shape of the sample introduced an error due to condensation of material on the inside of the doughnut hole; a correction was made for this error. The weight loss was determined by the use of a sensitive balance. Although the authors claim an error of $\pm 5\%$ in the pressures measured, the data does require some interpretation since there appears to be an uncertainty in the area of the condensation surface. The data presented involved an error of $\pm 5\%$ in the mass loss, and $\pm 5^\circ\text{K}$ in the temperature.

d. Langmuir, Jones and MacKay (References 9 and 10) reported the measurement of the vapor pressure by a free evaporation from nickel filament. The temperature was measured with a pyrometer and an emissivity of 0.36 was assumed for the nickel at temperature. This assumption leads to an error in the determination of the temperature.

There is another error due to the determination of the length of wire at temperature. Although estimates on the limits of these errors could be determined, the data herein falls out of the statistical limits which were set for use of the data in obtaining the best values of the heats of vaporization and vapor pressures by the third law method.

e. Morris et al (Reference 11) measured the vapor pressures of liquid nickel by a gas transport method utilizing an inert gas, such as helium, as the transport gas. The metal vapor was condensed onto the inner surface of the gas outlet tube. The gas flow rates were determined by a wet gas meter. The temperature was controlled to $\pm 5^\circ\text{K}$ and was determined by means of an optical pyrometer. Corrections for absorption of the radiation by the windows were made. A colorimetric method was used to determine the weight of nickel deposited by the gas stream. The possible errors in the spectroscopic determination of the nickel carried by the gas were not evaluated. The error in the volume of the gas gives a proportional percentage error in the vapor pressure. The probable error in the gas volume is less than 1%.

f. Bryce (Reference 12) also determined the vapor pressure of nickel by the vaporization of a filament using a target to catch the nickel vapor. The nickel condensed on the target was determined by a chemical technique. No further data is available on this technique.

g. Grimley et al (Reference 41) determined the vapor pressure of nickel during the course of a mass spectrometric investigation of the vaporization behavior of nickel oxide by combining the Knudsen cell effusion technique with a mass spectrometer. The temperature was determined by sighting on black body holes in the Knudsen cell. No information was given on the possible temperature gradients in the cell. There was some evidence that a reaction took place in the Knudsen cell which was made from aluminum oxide. There is no evidence that this reaction affected the measured vapor pressure or the observed heat of vaporization of nickel.

Since a mass spectrometer was used to determine the vapor pressure, a discussion of this technique is given in Appendix B, Section 2.

Grimley et al (Reference 4) used incorrect ionization cross sections for the ionization of the molecular and atomic species involved. The error in the ionization cross section of silver as noted in Appendix B, Section 2, introduces an error in the geometric factor defining the number of atoms which are in the volume defined by the electron beam. Other errors were made by these authors in reducing their data by the third law technique, for example, the use of values of the free energy functions of NiO which were inconsistent with available molecular data. A discussion of this paper is given in Part II, Section 2B.

B. Estimate of Second and Third Law Heats of Vaporization

Although a statistical technique has been reported (References 13 and 14) for obtaining "best values" of "second" and "third law" heats of vaporization from vapor pressure data obtained from a series of experiments, and from a number of different laboratories or sources, in this report a technique (Reference 15) proposed by Paule and Mandel was utilized which differs noticeably from the one they used in (References 13 and 14).

The first step in obtaining the "best value" was to examine the data of the individual laboratories for internal consistency, and also for consistency with other available experimental data, and, for information about the experimental techniques used as noted above, p. 21. In the "second law" treatments of the experimental data, the data from each laboratory was fitted by a least squares method to the Equation 6

$$\ln P = A + \frac{B}{T} \quad (6)$$

where P is the pressure (Torr) and $B = (\Delta H_T^\circ/R)$; ΔH_T° is the heat of vaporization at the temperature \bar{T} , where \bar{T} is the mean inverse temperature calculated by $\bar{T} = \left(\frac{1}{n_i} \sum \frac{1}{T_j} \right)^{-1}$; T_j is the temperature of the j -th data point, and n_i is the number of data points reported by the i -th laboratory.

All reported pressures having a deviation from the calculated values of the pressure which were greater than 2σ (σ = r.m.s. deviation) were eliminated from the original reported data in determining the least squares value of the slope.

(1) Determination of Second Law $(\Delta H_0^\circ)_v$, B and A

The composite best value of $(\Delta H_0^\circ)_v$ determined by means of the "second law", that is, the slopes of the various curves was obtained by first correcting the determined value of (ΔH_1°) to ΔH_0° . The corrections were made by using the enthalpy tables of Stull and Sinke (Reference 16), which are almost identical to those in References 3, 17, and 18, since all tables round off to the same values to the second decimal place. The list of data used in this determination is given in Table V.

Before applying the "least squares" treatment to the data of the individual laboratories, the data was examined for signs of "systematic errors" or "non-random errors" by arranging the deviations of the pressures in ascending order and plotting the deviations on probability paper. In all cases the data formed several groupings which could be fitted with straight lines. The deviations of the plots from a single straight line was not limited to the end points, thus indicating that the errors were "non-random" (Reference 19 and 20).

The best values of A and B of equation 6 for each individual set of data were determined by successively eliminating data points whose deviations between the measured and calculated values of the pressure were greater than 2σ (r.m.s. deviation). In some cases more than one recalculation was necessary, thus indicating a lack of statistical homogeneity in the data.

The composite best values of A and B were obtained by utilizing the statistical treatment described in (Reference 15) to determine the applicable weighing factors in averaging the values of ΔH_0° derived by the least squares treatment. The treatment in (Reference 15) is an attempt to weigh the effect of deviations between the individual laboratory's "best values", and the "within the laboratory" deviations; the individual weighing factors were calculated as follows.

1. To calculate the quantity defined in (Reference 15) as the mean square deviation within laboratory data, it is necessary to consider the fact that r.m.s. value of the slope is determined by (n_i-1) quantities where n_i is the number of data points reported by laboratory i . The mean square deviation of the "within" laboratories data is defined by the quantity MS_W .

$$MS_W = \frac{\sum_i (n_i - 2) \sigma_i^2}{N - k} \quad (7)$$

where k is the number of laboratories, σ_i^2 is the variance of the slope calculated for laboratory i , (n_i-2) is the number of degrees of freedom in determining the variance σ_i^2 of the slope, and $N = \sum_i (n_i - 2)$. This quantity MS_W is then assumed to be an estimate of the value of the "average" or within laboratory variance σ_W^2 of the slope. Another quantity which must be defined is the between laboratories variance of the slopes B .

$$MS_b = \frac{\sum_i (n_i - 1) (B_i - \tilde{B})^2}{k - 1} \quad (8)$$

In (Reference 8) B_i is the slope obtained for data of i -th laboratory and \tilde{B} is the average obtained by weighing the best slope for each laboratory as follows:

$$\tilde{B} = \frac{\sum_i (n_i - 1) B_i}{\sum_i (n_i - 1)} \quad (9)$$

It is assumed that the best composite value of the slope, $[B]$, can be determined from the weighted average of individual slopes defined by:

$$[B] = \frac{\sum_i \omega_i B_i}{\sum_i \omega_i} \quad (10)$$

where ω_i is a weighing factor which is further defined by the following relation:

$$\omega_i = \left[\lambda + 1 / (n_i - 1) \right]^{-1} \quad (11)$$

where

$$\lambda = \sigma_b^2 / \sigma_W^2 \quad (12)$$

The best value of λ is obtained by an iterative procedure which gives a value of $G = 0$ for the following relation:

$$G = \sum_i \omega_i (B_i - [B])^2 - (k-1) \sigma_W^2 \quad (13)$$

The first estimate of λ and thus the first guess of the weighing factors, ω_i is obtained from the relations given for α_W^2 above and the following relation for σ_b^2 :

$$\sigma_b^2 = \frac{MS_b - MS_W}{\left[\sum_i (n_i - 1) - \frac{\sum_i (n_i - 1)^2}{\sum_i (n_i - 1)} \right] / k - 1} \quad (14)$$

Subsequent values of λ are then estimated until Equation 13 equals 0 to the desired approximation.

The best value of $(\Delta H_0^\circ)_v$, the heat vaporization of nickel solid, which was obtained by utilizing the above statistical method, was:

$$(\Delta H_0^\circ)_v (s \rightarrow v) = 102.9 \pm 4.2 \text{ kcal/mole.}$$

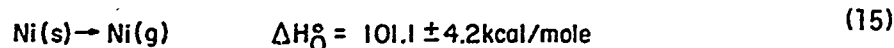
It was also of interest to obtain the value of B for a given temperature range so that Equation 6 may be used to calculate vapor pressures. Since the data utilized covers the temperature range 1273 to 1709°K, a value of B at the midpoint of this range was calculated. It should be noted that there is a difference in specifying the average temperature for the range, 1491°K, as the midpoint, and the average temperature that is derived from the reduction of a set of data by the least squares technique. The value of $B(1491^\circ\text{K}) (= \Delta H_{1491}^\circ / R)$ is given by correcting ΔH_0° to ΔH_{1491}° . This was done by using the enthalpy tables (Reference 16) to obtain a value of $\Delta H_{1491}^\circ = 101.1 \pm 4.2 \text{ kcal/mole.}$

There is a maximum error of 0.65 kcal over the temperature range introduced by assuming that ΔH° is constant over the range. The error of 0.65 kcal is the systematic error at the end points of the range; to a good approximation the total error over the range may be estimated as $\pm 4.9 \text{ kcal}$. Therefore, the average value ΔH° (1273 to 1709°K) is given as $101.1 \pm 4.9 \text{ kcal/mole}$ and the value of $B = 50,884 \pm 2,466$ over the range.

An estimate of the intercept A was also made using the same statistical treatment which was used in deriving the value of B. In deriving the value A, however, the data of Morris, et al (Reference 11) was omitted since this data refers to the liquid vaporization. Furthermore, since the parameters in Equation 6 must relate to a temperature range which does not involve a discontinuity in the parameters, such as caused by a phase change two values of A and B were calculated which can be used to calculate the vapor pressure over the whole temperature range for which data is available.

The "best values" from the second law determinations for A and B for both the solid and liquid ranges are given by Equations 15 to 18.

For the reaction



and the vapor pressure over the temperature range 1273 to 1709°K is:

$$\ln P_s (\text{Torr}) = 24.26 \pm 1.39 - \frac{50,884 \pm 2,466}{T} \quad (16)$$

For reaction:



there is only one value of ΔH° which was obtained from data in Reference 11. This data was statistically treated to eliminate pressure data points which deviated more than 2σ (r.m.s. deviation) from the calculated values. This treatment yielded the following values of $A = 22.222$, and $B = 48,271$. These values differ slightly from the values of $A = 22.314$ and $B = 48,432$, reported in (Reference 11). The best equation for the vapor pressure of liquid nickel in the temperature range 1816 to 1895°K is:

$$\ln P_l (\text{Torr}) = 22.222 \pm 0.29 - \frac{48,271 \pm 533}{T} \quad (18)$$

In subsequent discussions covering the third law "best values," relations between A and the free energy functions will be discussed.

TABLE VI
QUANTITIES USED IN DETERMINING SECOND LAW "BEST VALUES"
OF ΔH_0° , B AND A FOR VAPORIZATION OF NICKEL (SOLID)

Reference	Number of Data Points- n_i	$(\Delta H_0^\circ)_i$ kcal/mole	Variance (a) $\sigma_i^2 (\Delta H_0^\circ)$	A	Variance (a) $\sigma_i^2 (A)$
(c)	24	115.83	5.48	27.861	3.389
(4)	18	112.36	1.56	26.735	0.144
(9)	10	102.21	0.34	24.092	0.0433
(12)	7	93.99	58.69	21.354	8.451
(10)	5	89.36	48.16	20.955	5.688
(11)	15	103.10	1.12	(b)	(b)

- (a) Statistical degrees of freedom equal (n_i-2) for each determination.
 (b) Liquid nickel, this value not used in averaging.
 (c) This report Part I.

(2) Determination of Third Law Best Values of B, A and ΔH_0°

Third law determinations of the "best values" of the quantities B, A and ΔH_0° can be made by utilizing the expressions for the free energy functions and the values of these functions given in (Reference 3); and the data reported in References (4 through 12). The data in References 5 through 7 were omitted because it was inconsistent with other data as noted above. The data in (Reference 10) was also omitted because the value of ΔH_0° obtained from this set of data deviated by more than 2σ from the average ΔH_0° obtained by simply statistically weighing the values of each set of data by the number of data points reported by each laboratory. Although this statistical test appears to be somewhat crude, it should be remembered that such an averaging process overestimates the variance and, therefore, represents a weaker test of nonhomogeneity and low probability of the validity of the data than the normally used χ^2 test which puts an upper and lower bound on the relative values of variances for rejecting observations. The reason that only an upper

bound was used, was simply due to the fact the data were statistically too inhomogeneous to treat by the χ^2 test which utilizes both upper and lower bound.

In order to compare the equation for $\ln P$ in the temperature range 1273 to 1709°K with that obtained by means of the second law as noted above, it is necessary to compare equations for $\ln P$ used to obtain third law values of ΔH° with that used to obtain the second law values of this quantity. In the use of the second law, the slope is equated to the quantity $(\Delta H^\circ/\bar{T})$ where \bar{T} is the temperature corresponding to the mean inverse temperature as noted above. Equation 5 used to obtain the value of ΔH_{298}° by the third law which can be expressed as follows:

$$R \ln P = \sum_{g-s} - \left(\frac{G^\circ - H_{298}^\circ}{T} \right) - \frac{\Delta H_{298}^\circ}{T} \quad (19)$$

To convert Equation 19 to the "second law" form, that is Equation 6

$$\ln P = A + \frac{B}{T} \quad (6)$$

the quantity $\left(\frac{\Delta H_{\bar{T}}^\circ - \Delta H_{298}^\circ}{T} \right)$ must be subtracted from and added to the righthand side of Equation 19 as follows:

$$R \ln P = \sum_{g-s} - \left(\frac{G^\circ - H_{298}^\circ}{T} \right) + \left(\frac{\Delta H_{\bar{T}}^\circ - \Delta H_{298}^\circ}{T} \right) - \frac{\Delta H_{298}^\circ}{T} - \left(\frac{\Delta H_{\bar{T}}^\circ - \Delta H_{298}^\circ}{T} \right) \quad (20)$$

This equation reduces to Equation 21. The tabulated values (References 3 and 16) of $(\Delta H_{\bar{T}}^\circ - \Delta H_{298}^\circ)$ being used to make the corrections

$$R \ln P = \sum_{g-s} - \left(\frac{G_{\bar{T}}^\circ - H_{\bar{T}}^\circ}{T} \right) - \frac{\Delta H_{\bar{T}}^\circ}{T} \quad (21)$$

As will be shown the quantity $\Sigma - \left(\frac{G_T^\circ - H_{298}^\circ}{T} \right)$, is almost constant over the temperature range of interest so that its average can be taken as the constant A which with the unit of pressure in Torr is given by

$$A = \Sigma_{g-s} \left(\frac{G_T^\circ - H_{298}^\circ}{RT} \right) + \frac{1}{RT} \int_{298}^{\bar{T}} \Delta C_p dT + \ln 760 \quad (22)$$

where $\Delta C_p = C_p \text{ (gas)} - C_p \text{ (solid)}$, and is a function of T.

The slope, B, is given by Equation 23

$$B = -\frac{\Delta H_{298}^\circ}{R} - \frac{1}{R} \int_{298}^{\bar{T}} \Delta C_p dT \quad (23)$$

The quantity $\int_{298}^{\bar{T}} \Delta(\Delta H^\circ)$ is a constant for a given mean temperature \bar{T} .

In this report all third law data was reduced by using the values of $-\left(\frac{G^\circ - H_{298}^\circ}{T} \right)$, given in Reference 3.

An estimate of the error in the tabulated free energy functions is limited to assuming that the error that is reported by Kelly (Reference 17) for enthalpies in this temperature range. This error is 0.3%. However, additional errors in A arise due to the fact that $\Sigma - \left(\frac{G_T^\circ - H_{298}^\circ}{T} \right)$ is not constant over the temperature range. The error due to this variation has also been evaluated by finding the mean value of this quantity for all determinations used and evaluating the r.m.s. deviation; to this quantity the estimated error in $[\Delta(\Delta H^\circ)]$ was added to obtain the total error.

The mean value of \bar{A} for the temperature range of interest to us is that at mean temperature $\bar{T} = 1535^\circ\text{K}$, which is the inverse mean temperature as defined on p. 22. This method of obtaining the mean temperature is consistent with the method of averaging the free energy functions, which are weighed by the quantity $(1/T)$. The error arising in the use of the average free energy function over temperature range 1250°K to

1710°K is not random, but can be expressed as a maximum limit of the error at the end points of the range. The maximum error over the range, including the 0.3% error in the free energy functions, is 1.5% while the average deviation is 0.7%. If it is wrongly assumed that the errors are random and the r.m.s. deviation is calculated, then an estimated error of 0.8% is obtained. The above is a statement of errors which arise in the use of the average value of $\bar{A} = 23.50$ at $\bar{T} = 1535^\circ\text{K}$. The value of $\Delta H_{1535}^\circ = 99.47 \pm 0.6$ kcal/mole, while $B = 50,060 \pm 301$. The best value of $\Delta H_0^\circ = 101.45 \pm 0.62$ kcal/mole. This value of ΔH_0° is more reliable than the second law value of 102.9 ± 4.2 kcal/mole even though they are nearly equal. The near equality appears to be fortuitous when one considers the range of the data used in the two determinations.

The best third law equation for the vapor pressure of solid nickel in the temperature range 1250°K to 1710°K is as follows:

$$\ln P_s (\text{Torr}) = 23.50 \pm 0.35 - \frac{50,600 \pm 301}{T}$$

The third law parameters of equation 6 can also be determined for liquid nickel from the limited amount of data available (Reference 11) in the temperature range 1816 to 1895°K. The best value of $A = 21.98$ with a mean error of ± 0.04 and maximum error at the end points of the temperature range of ± 0.05 . The value of $B = 47,775 \pm 138$ (mean error) with a maximum error ± 210 . As pointed out above there are systematic errors in assuming that A and B are constant over the temperature range so that the maximum errors represent the errors at the end points. The third law equation for the liquid vapor pressure is then given by:

$$\ln P_l (\text{Torr}) = 21.98 \pm 0.05 - \frac{47,775 \pm 210}{T}$$

in the temperature range 1816 to 1895°K.

An interesting aside was the treatment of the third law data points to obtain a composite second law value of ΔH_0° by successively eliminating data points whose deviations were greater than 2σ . Starting with all the original points reported, i.e. 91 points, it was found that after a number of trials only 26 points remained which were from the following sources: References 4, 8, and 12. A value of $\Delta H_0^\circ = 99.3 \pm 0.38$ kcal/mole was obtained. This calculation further indicated the lack of statistical homogeneity in the composite data.

TABLE VII
THIRD LAW VALUES OF ΔH_0° USED TO CALCULATE
"BEST THIRD LAW VALUE" FOR Ni(s)→Ni(g)

Reference	n_i (b)	ΔH_0° kcal/mole	$\sigma_i(\Delta H_0^\circ)$ deviation kcal/mole	variance $\sigma_i^2(\Delta H_0^\circ)$
Part I	25	102.63	2.09	4.368
(4)	16	101.29	0.13	0.0169
(8)	12	100.74	0.20	0.04
(12)	7	100.28	0.84	0.7056
(11)	16	102.12	0.07	0.0049
(5-7) ^a	10	73.60	0.66	0.4356
(10 ^a)	5	96.76	1.45	2.103
Best Value		101.45	0.62	0.38

(a) Not used in determining final value of ΔH_0° .

(b) n_i - number of determinations used after eliminating those with deviation $>2\sigma$.

Since there are differences between the statistical treatments of data reported herein and that reported by Paule and Mandel (References 13 and 14) a discussion of these differences is in order. The differences in the statistical treatments arise from the fact the data available on the vapor pressure of nickel lacks statistical homogeneity and thus a composite value of the second and third law heats of vaporization could not be generated by simply treating all the data as a single set of data and obtaining best value. The treatment which was used takes into account the nonhomogeneity of the data by statistically weighing the

results of the individual laboratories which were used in generating an over all "best value". The statistical test used for rejecting data in this report is a deviation of the observed data of more than 2σ (r.m.s. deviation). Paule and Mandel (References 14 and 15) used as F test which in essence put limits on the probability between 0.975 and 0.025 on the validity of the data they used. Although a 2σ error limit does not take into account the number of degrees of freedom for each curve in setting error limits, it does give a convenient limit to the maximum deviation to be tolerated which has been used by other authors (References 21 and 22).

The probability for the value of t ($\text{deviation}/\sigma$) > 2 was between 5 and 15% with a large proportion of the cases being between 5 and 10% (Reference 22). Therefore in general this validity limit is not inconsistent with the other statistical treatments that were done. It is interesting to note that with continued elimination of data points whose deviations are greater than 2σ there is a reduction in the number of statistical degrees of freedom and the probability that a given value will fall outside of the 2σ limit changes. However, it is also important to note that by definition the homogeneity (a measure of self-consistency) of a given data point is measured by $t = (\text{deviation}/\sigma)$.

SECTION 2 Thermodynamics of Nickel Oxide Vaporization

In the course of reducing the available data on the vaporization of NiO , Grimley, et al (Reference 4) derived a value for heat of dissociation of the diatomic molecules $\text{NiO}_{(g)}$. The heat of dissociation thus obtained appears to add consistency to the values of heats of vaporization of $\text{Ni}_{(s)}$ which were reported. Since this data has appeared, additional data has been reported on the free energies and enthalpies of the reactions 19-23, which form a closed cycle.

References		ΔH_0° kcal/mole	
4	$\text{NiO}_{(s)} \rightarrow \text{NiO}_{(g)}$	124.4 ± 0.4 (a)	(19)
4	$\text{NiO}_{(g)} \rightarrow \text{Ni}_{(g)} + \text{O}_{(g)}$	92.7 ± 0.9 (a)	(20)
(b)	$\text{Ni}_{(g)} \rightarrow \text{Ni}_{(s)}$	-101.5 ± 0.6	(21)
28	$\text{O}_{(g)} \rightarrow 1/2 \text{O}_{2(g)}$	$-58.969 \pm .005$	(22)
23 to 27	$\text{Ni}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{NiO}_{(s)}$	$-56.67^{(25)} \pm .13$	(23)

(a) Corrected values of data in Reference 4. See p. 42 of this report.

(b) Best composite value. See p. 30.

The new data for the change in enthalpies (reactions 19-23) was used in conjunction with data of Reference 4 on the vapor pressure of $\text{NiO}_{(s)}$ to obtain the best value of the heat of dissociation of $\text{NiO}_{(g)}$. The reported data (Reference 4) on the observed partial pressures of the various gaseous species in equilibrium with $\text{NiO}_{(s)}$ were corrected by using new values of ionization cross sections, Appendix B, and new values of free energy functions for $\text{NiO}_{(g)}$ and $\text{NiO}_{(s)}$. The standard state to which the thermodynamic functions were referred was 0°K. Since many thermodynamic functions are referred to 298.13°K, these functions had to be corrected to a 0°K reference state.

A. Thermodynamic Functions of Solid Nickel Oxide (NiO_s)

The value of $(H^\circ_{298.13} - H^\circ_0)$ for $\text{NiO}_{(s)}$ was obtained using the heat capacity data reported by King (Reference 29). This data is given in Table III. A calculation was made to determine the difference in enthalpy of $(\text{NiO})_s$ between 54.28°K and 0°K. This was done by extrapolating the data in Reference 4 by the use of the following expression for the enthalpies:

$$H_T^\circ - H_0^\circ = D\left(\frac{404}{T}\right) + E\left(\frac{620}{T}\right), \quad \text{where } D\left(\frac{404}{T}\right) \text{ (References 30 and 31) is the}$$

Debye-Enthalpy Function and $E\left(\frac{620}{T}\right)$, (Reference 31), the Einstein-Enthalpy Function. The number (404) is an apparent value of the Debye

temperature and (620) is an apparent value of the Einstein temperature. This calculation gave a value for $(H_{54.28}^{\circ} - H_0^{\circ}) = 11.56$ cal/mole. The quantity $(H_{298.13}^{\circ} - H_{54.28}^{\circ})$ was calculated by adding increments of enthalpy over limited temperature intervals. Taking the average value of the heat capacity, C_p , over the interval defined by points (n+1) and (n), where n represented a point in the numerical sequence, the enthalpy difference between T_{n+1} and T_n was:

$$(H_{T_{n+1}} - H_{T_n}) = \left(\frac{C_{p_{n+1}} + C_{p_n}}{2} \right) (T_{n+1} - T_n) \quad (24)$$

The sum of the enthalpy increments between any two temperatures gives the enthalpy difference between the temperatures. This procedure as noted gave $(H_{298}^{\circ} - H_0^{\circ}) = 1609.58$ cal/mole. i.e.

$(H_{298.13}^{\circ} - H_{54.28}^{\circ}) = 1598.02$ cal/mole; adding to this the quantity $(H_{54.28}^{\circ} - H_0^{\circ}) = 11.56$ cal/mole, a value of $(H_{298.13}^{\circ} - H_0^{\circ}) = 1609.58$ cal/mole was obtained.

The free energy functions of $NiO_{(s)}$: $[-(G_T^{\circ} - H_0^{\circ})/T]$ i.e.

$$-(G_T^{\circ} - H_0^{\circ})/T = S_T^{\circ} - (H_T^{\circ} - H_0^{\circ})/T,$$

were calculated from tabulated and extrapolated values of standard entropy S_T° , at the temperature T, and the enthalpy difference expressed as $(H_T^{\circ} - H_0^{\circ})/T$ (Reference 18). Since enthalpy data is tabulated as $(H_T - H_{298}^{\circ})$, a correction as detailed above was applied giving the thermodynamic data used, as shown in Table IX.

B. Calculation of Thermodynamic Functions of $NiO_{(g)}$

The thermodynamic functions of $(NiO)_g$ were calculated by assuming that the NiO gas molecule is a perfect gas composed of diatomic rigid-rotor-oscillators as in the case of Ni_2 (Appendix A). The contributions of the individual degrees of freedom of the possible motions of the molecule to the free energy function were determined. The contribution

TABLE VIII
HEAT CAPACITIES OF NiO_(s)

T, °K	C _p ^(a) cal/°K/mole	ΔT, °K (T _{n+1} -T _n)	\bar{C}_p , cal/°K/mole (C _{p,n+1} +C _{p,n})/2	(ΔH _{T_{n+1}} ^o -H _{T_n} ^o) cal/mole
54.28	0.900	4.65	1.006	4.678
58.93	1.112	4.56	1.227	5.595
63.49	1.341	4.61	1.462	6.740
68.10	1.582	4.37	1.700	7.429
72.47	1.818	4.27	1.935	8.262
76.74	2.051	3.48	2.150	7.482
80.22	2.248	3.59	2.346	8.422
83.81	2.444	10.85	2.750	29.84
94.66	3.056	10.31	3.348	34.52
104.97	3.639	9.60	3.899	37.43
114.57	4.158	10.03	4.425	44.38
124.60	4.691	11.28	4.980	56.17
135.88	5.269	9.67	5.503	53.21
145.55	5.737	10.31	5.979	61.64
155.86	6.221	9.92	6.430	63.79
165.78	6.639	10.06	6.840	68.81
175.84	7.041	9.94	7.234	71.91
185.78	7.427	10.16	7.606	77.28
195.94	7.785	10.19	7.960	81.11
206.13	8.134	10.06	8.296	83.46
216.19	8.457	9.66	8.610	83.17
225.85	8.762	10.22	8.906	91.02
236.07	9.050	9.56	9.178	87.74
245.63	9.306	10.66	9.452	100.76
256.29	9.597	9.86	9.721	95.85
266.15	9.845	9.86	9.963	98.24
276.01	10.08	10.42	10.20	106.28
286.43	10.32	9.51	10.44	99.28
295.94	10.55	2.21	10.55	23.52

$$H_{298.13}^{\circ} - H_{54.28}^{\circ} = 1598.02$$

$$H_{54.3}^{\circ} - H_0^{\circ} = 11.56^{(b)}$$

$$H_{298.13}^{\circ} - H_0^{\circ} = 1609.58 \text{ cal/mole}^{(c)}$$

(a) Reference 29.

(b) Calculated by using the following expression for the enthalpy utilizing Debye functions and Einstein functions:

$$D\left(\frac{422}{54.3}\right) + E\left(\frac{585}{54.3}\right)$$

(c) Johnston and Marshall (Reference 8) report $H_{298.13}^{\circ} - H_0^{\circ} = 1630$ cal, using data H. Seltz, J. DeWitt, H.J. McDonald (Reference 33) with expression for

$$C_p = D\left(\frac{404}{T}\right) + E\left(\frac{620}{T}\right), \text{ between } 0^{\circ}\text{K and } 68^{\circ}\text{K.}$$

TABLE IX
FREE ENERGY FUNCTIONS FOR $\text{NiO}_{(s)}$ (REFERENCE 18)

$T^{\circ}\text{K}$	$-(G_T^{\circ}-H_0^{\circ}/T)_s$ cal/ $^{\circ}\text{K}/\text{mole}$
1500	18.43
1600	19.19
1700	19.91
1800	20.61

to the free energy functions by the translational degrees of freedom, $-(G_T^{\circ}-H_0^{\circ}/T)_t$, is given by Equation 41. The rotational partition function was determined by utilizing Equation 43, and noting that the symmetry number $\sigma = 1$, and that the rotational constant has the value given in Table IX. The electronic contribution is given by Equation 42. The electronic partition function required for Equation 42 was determined as noted in the next paragraph utilizing the energy levels given in Table X.

(1) Estimate of Electronic Contribution to $(\text{NiO})_g$ Partition Function

In determining the electronic contribution to the partition function of NiO molecule, and subsequently to the thermodynamic functions, the degeneracy (statistical weight) of the spectroscopic state (electronic energy level) must be determined. Previous estimates of the partition functions were incorrect, because the spectroscopic states of NiO were considered to be derived from the nickelous ion (Ni^{++}) (Reference 36), therefore it is necessary to redescribe the atomic and molecular binding in the diatomic molecule NiO in order to re-estimate the partition function.

The assumption made in Reference 36 that the (NiO) molecule is ionic ignored the preponderance of the evidence on the electronic characteristics of diatomic molecules which indicates that most diatomic molecules do not exist as ionic molecules (Reference 37). Therefore, the description of the electronic states of the NiO diatomic molecule which must be used are those consistent with the electronic states of atomic molecules. To test the idea that (NiO) is atomic, the instability of the ionic

TABLE X

FREE ENERGY FUNCTIONS OF $\text{NiO}_{(g)}$

T °K	$-\left(\frac{G^\circ - H^\circ}{T}\right)_{\text{Rot} + \text{trans}}^{(b)}$	$-\left(\frac{G^\circ - H^\circ}{T}\right)_v^{(a)}$	$-\left(\frac{G^\circ - H^\circ}{T}\right)_{\text{el}}^{(b)}$	$-\left(\frac{G^\circ - H^\circ}{T}\right)_{\text{total}}$
	cal/°K/mole	cal/°K/mole	cal/°K/mole	cal/°K/mole
100	36.66	0.00	0	36.66
200	43.48	0.02		43.50
298.13	46.24	0.11		46.35
300	46.30	0.12		46.42
400	48.30	0.23		48.53
500	49.85	0.37		50.22
600	51.12	0.52		51.64
700	52.19	0.66		52.85
800	53.12	0.80		53.92
900	53.94	0.93		54.87
1000	54.67	1.06		55.73
1100	55.33	1.18		56.51
1200	55.94	1.29		57.23
1300	56.50	1.40		57.90
1400	57.0	1.51		58.52
1500	57.49	1.61		59.10
1600	57.94	1.70		59.64
1700	58.36	1.79		60.15
1800	58.76	1.88		60.64
1900	59.13	1.96		61.09
2000	59.49	2.05		61.54

(a) Vibrational frequency $\omega = 615 \text{ cm}^{-1}$ (Reference 34).

(b) Electronic levels: $V_{\text{el}} = 12,725$ and $16,447 \text{ cm}^{-1}$ (Reference 34).
Rotational constant $B = 0.41 \text{ cm}^{-1}$ (Reference 35).

structure (Ni^{++}O^-) with respect to the separated ions $[\text{Ni}^{++} + \text{O}^-]$ ion had to be determined.

This was done by taking the difference [6.15 ev] between the ionization potential of Ni atom, $I(\text{Ni}) = 7.61 \text{ ev}$ (Reference 38) and electron affinity of O atom, $E(\text{O}) = 1.465 \text{ ev}$ (Reference 6). This difference is too large to form a stable ionic molecule. An example of a stable ionic molecule is $[\text{Na}^+ \text{Cl}^-]$, the difference, $[I(\text{Na}) - E(\text{Cl})]$ being only

1.40 ev (Reference 40). The molecule $[Ni^{++}O^{--}]$ is even more unstable than $[Ni^{+}O^{-}]$ since $I(Ni^{+}) = 18.2$ ev (Reference 28) and $E(O^{-}) = \text{zero}$ (Reference 39).

Thus the total difference in the quantity $[I-E]$ in going to the second ionization potential of Ni, to form $[Ni^{++}]$ and to the second electron affinity of oxygen to form the $[O^{--}]$, species is $[25.81 - 1.465]$ ev or 24.34 ev. This difference is obviously too large for the molecule $[Ni^{++}O^{--}]$ to be stable with respect to the covalent $NiO(g)$ molecule.

To test further the validity of the atomic molecular structure for $[NiO]$ the ionicity of the $[NiO]$ molecule was estimated by taking the difference between the average heats of dissociation of the diatomic molecules of the elements and the heat of dissociation of gaseous NiO . The heat dissociation used for Ni_2 was that found by recalculating Kant's data, (Reference 42) i.e. $D_0^{\circ}(Ni_2) = 61$ kcal/mole (p. 52). The heat of dissociation of O_2 used was that used whenever electronegativities are used in conjunction with thermodynamic data and is equal to the heat of dissociation of two single bonds, i.e. 66.5 kcal instead of the measured $D_0^{\circ} = 118$ kcal/mole (Reference 45). The heat of dissociation of NiO was estimated as 85 kcal (Reference 4). Defining Δ , as a measure of the ionicity, one finds that for $[NiO]$:

$$\Delta = 1/2 D_0^{\circ}(O_2) + 1/2 D_0^{\circ}(Ni_2) - D_0^{\circ}(NiO) = 21 \text{ kcal},$$

or that the ionicity is relatively low.

Having concluded that ionicity of NiO is low one is lead to assumptions concerning the nature of the ground electronic state of $[NiO]$. Such assumptions can be made on the basis of the observed electronic transitions. However, since these transitions have not been classified for NiO , one must guess at the electronic configuration of the NiO molecule. The ground state could be classified either as a $^1\Sigma$ or $^1\Delta$ configuration since these are possible electronic configurations of combined $[O]$ and $[Ni]$ atoms, which have been determined by taking the possible combination of atomic states as given by Herzberg (Reference 44). The assumption that the ground state should be a $^1\Sigma$ state leads to the

assumption that the excited states should be designated as $^1\Sigma$ states. This labeling is the most consistent with our ignorance and information, and it does not appear to violate any selection rules nor is it contrary to any spectroscopic observations. Having re-estimated the values of the electronic partition functions by using the expressions given in Table XIII; other available molecular data was used to recalculate the free energy function of NiO as illustrated in Table X.

TABLE XI
CORRECTED PRESSURES OF NiO_(g) AND
THIRD LAW HEATS OF VAPORIZATION: NiO_s → NiO_g (a)

T°K	Pressure ^(a) atm	ΔH_0° kcal/mole
1575	28.59×10^{-10}	125.35
1587	56.92×10^{-10}	124.09
1596	53.46×10^{-10}	124.97
1606	8.52×10^{-9}	124.22
1624	10.90×10^{-9}	124.76
1625	11.35×10^{-9}	124.70
1630	13.91×10^{-9}	124.10
1646	20.70×10^{-9}	125.16
1651	23.53×10^{-9}	124.29
1657	24.68×10^{-9}	124.32
1659	28.52×10^{-9}	124.14
1673	37.82×10^{-9}	124.20
1673	36.22×10^{-9}	124.35
1679	42.18×10^{-9}	124.30
1679	46.86×10^{-9}	123.93
1684	45.26×10^{-9}	124.38
1684	47.62×10^{-9}	124.21
1707	7.69×10^{-8}	124.20
1709	51.92×10^{-9}	125.68 ^(b)

(a) Pressures = 0.641 x Pressures reported in Reference 4.

(b) Omitted from final determination of ΔH_0° as shown on p. 41.

C. Examination of the Data on the Enthalpy of Vaporization of $\text{NiO}_{(s)}$

Since the only available data on the partial pressures of $\text{NiO}_{(g)}$ in equilibrium with $\text{NiO}_{(s)}$ is that reported in Reference 4, this data was examined, and as noted in Appendix B-1, the reported pressures were corrected for the latest data available on ionization cross sections. The corrected data on the equilibrium partial pressure of $\text{NiO}_{(g)}$ for Equation 19 is given in Table XI as well as the heats of vaporization calculated by the third law. Utilizing the statistical criteria as given in Part II, Sec B1 and B2, a best value of $\Delta H_0^\circ = 124.4 \pm 0.4$ kcal was obtained. By utilizing the relations indicated in Part II, Sec B2, values of the parameters A and B for the vapor pressure equations were also calculated by averaging the values of the free energy functions, over the temperature range, 1575 to 1707°K, taking a value of $\bar{T} = 1646^\circ\text{K}$, and correcting the third law values of ΔH_0° to ΔH_{1646}° . The equation for the vapor pressures of $\text{NiO}_{(g)}$, in equilibrium with $\text{NiO}_{(s)}$, can thus be expressed as

$$\ln P_{\text{Torr}}(\text{NiO})_g = 25.52 \pm 0.05 - \frac{60,188 \pm 470}{T} \quad (25)$$

The error limits were set by the observed error in ΔH_0° plus the reported error of 0.4% in the enthalpy of solid (Reference 17). The error in A is systematic since it is temperature dependent; at the extremes of the temperature range, 1575°K, it is equal to +0.16, and at 1709°K it is equal to -0.13.

A redetermination of the second law, ΔH_0° , of reaction (Reference 19) was also performed. The best least squares value obtained for $\Delta H_{1646}^\circ = 127.6 \pm 3.1$ kcal/mole. The best value of $\Delta H_0^\circ = 133.3 \pm 3.2$ kcal per mole. The best value of the parameters A and B are shown in the vapor pressure equation (Reference 26).

$$\ln P_{\text{Torr}}(\text{NiO})_g = 27.92 \pm 0.96 - \frac{64,243 \pm 1576}{T} \quad (26)$$

The discrepancies between the second and third law values of the parameters in the vapor pressure equation appear similar to those obtained for nickel, Part II, Sec B1 and B2. Due to the greater consistency of the third law determinations, the third law values were adopted as the best values. Tables X and XI show the data used in determining the third law parameters. Grimley (Reference 4) reported value of $\Delta H_0^\circ = 129.5 \pm 5$ kcal/mole. The vapor pressure data of Johnston and Marshall (Reference 8) on NiO, was not utilized in this case because there was difficulty in differentiating between the loss of weight from the sample due to NiO_(g) and that due to Ni_(g), leaving doubt as to the accuracy of the results.

D. Examination of the Data on the Heat of Formation of NiO_(s)

To complete the evaluation of the available information of the enthalpy changes for Reactions 19 to 23 an examination of the available data on the heats of formation NiO_(s) (Reaction 23) was performed. In the process of performing this evaluation, the mass spectrometric data of Grimley, et al (Reference 4) on the partial pressure of O₂ was corrected by utilizing new information on the ionization cross sections of O₂ and O (see Appendix B-1).

Table XII, lists the O₂ pressures reported by Grimley corrected for errors in the ionization cross sections as noted in p. 67. On the basis of this data and utilizing the second and third law methods for determining heats of dissociation of NiO_(s) as per Equation 23, the values obtained were as follows: $\Delta H_0^\circ = 57.37 \pm 0.30$ kcal/mole; $\Delta H_{298}^\circ = 57.94 \pm 0.30$ kcal/mole. The best literature value of $\Delta H_{298}^\circ = 57.240 \pm 0.13$ kcal; and that of $\Delta H_0^\circ = 56.67 \pm 0.13$ kcal/mole. Reference 26.

It is of interest to note that the r.m.s deviation of Grimley's corrected values of the oxygen pressures from the best values of these pressures reported in Reference 26 is 42%. The comparison was made by interpolating the pressures reported in Reference 26 for the temperatures reported by Grimley (Reference 4). This relatively good agreement between the mass spectrometric technique and the high temperature E.M.F. techniques utilized in obtaining the data analyzed by Kellogg (Reference 26), gives

TABLE XII

CORRECTED DATA FOR REFERENCE 4 O₂ PRESSURES
AND THIRD LAW ΔH_f° FOR REACTION: $\text{Ni}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{NiO}_{(s)}$

Temperature °K	Pressure O ₂ ^(a) Torr	ΔH_0° kcal/mole
1575	1.74×10^{-4}	-57.87
1587	2.58 "	-57.65
1596	2.76 "	-57.85
1606	3.31 "	-57.93
1624	7.43 "	-57.23
1625	6.22 "	-57.55
1630	6.98 "	-57.52
1646	1.02×10^{-3}	-57.47
1651	1.24 "	-57.24
1657	1.64 "	-57.04
1659	1.44 "	-57.29
1673	1.88 "	-57.31
1673	1.95 "	-57.26
1679	2.12 "	-57.34
1679	2.47 "	-57.08
1684	2.58 "	-57.16
1684	3.14 "	-56.83
1707	4.01 "	-57.17
1709	4.02 "	-57.25

$(\Delta H_0^\circ)_f (\text{NiO}) = -57.37 \pm 0.30$ kcal/mole.

(a) Pressure of O₂ = 1.25 Pressure O₂ in Reference 4.
see p.67.

confidence that the mass spectrometer can be used to determine quantitatively the flux from a Knudsen cell and thus the pressure inside the cell.

Determination of $D_0^\circ(\text{NiO}_g)$

The determination of $D_0^\circ(\text{NiO})_g$ as per Equation 20 is now reduced to completing the thermodynamic cycle defined by Equations 19 through 23. The best value of $D_0^\circ(\text{NiO}) = 92.7 \pm 0.9$ kcal/mole. The error in D_0° being determined as the r.m.s. of the sum of the squares of percentage errors of the quantities in the cycle.

It should be noted that although the value of $D_0^\circ (\text{NiO}) = 92.7 \text{ kcal/mole}$ differs from the value of $D_0^\circ = 86.5 \text{ kcal}$ reported in Reference 4, it is still consistent with this and other reported values: $D_0^\circ = 87 \text{ kcal}$ suggested by Trivedi (Reference 45) and $D_0^\circ < 4.2 \text{ ev}$ (96.6 kcal/mole) suggested by Huldt and Lagerquist (Reference 35).

PART III

APPENDIX I

DETERMINATION OF D_0° FOR Ni_2

It was necessary to obtain a value of the dissociation energy, D_0° , for the Ni_2 molecule in order to justify the assumption that the ground state of NiO is a $^1\Sigma$ state. A survey of the literature indicated that Kant(Reference 42) had made the only reported determination of $D_0^\circ(Ni_2)$. The data reported by Kant was critically examined, and several errors were noted in the data reduction, therefore, the reported data had to be reconciled with the reported results. For example, Kant(Reference 42) reported that the experimentally determined ratios of the mass numbers which he stated contributed most significantly to the composition of the gas phase Ni_2 (Ni_2^{116} , Ni_2^{118} , and Ni_2^{120}) were as follows 116:118:120 = 1.0:0.77:0.15, and he further stated that these ratios corresponded to that expected from known isotopic distribution. As shown in the following analysis these ratios are not what is expected from isotopic distribution in the natural abundance. An examination of the natural isotopic abundance of nickel gives the following isotopic distribution: Ni^{58} - 67.88%; Ni^{60} - 26.32%; Ni^{61} - 1.19%; Ni^{62} - 3.66%; and Ni^{63} - 1.08% (Reference 46). These ratios in turn can be used to determine the ratio of diatomic molecules of various isotopic composition either by statistical determination of the distribution, or from the ratio of the equilibrium constants for the reactions for the dissociation of the diatomic molecules such as:



The equilibrium constants for these reactions differ from each other by the symmetry numbers σ_{ij} where $\sigma_{ii} = 2$ for homonuclear molecules, and $\sigma_{ij} = 1$ for heteronuclear molecules. The equilibrium constant for the reactions involving the isotopes i, j are equal to (K/σ_{ij}) where K is the equilibrium constant for reactions involving isotopes for which $i \neq j$ (References 47 and 48). Equilibrium constants and reactions for all the isotopic combinations of i and j can be written by simply rotating i and

j, over all the possible values of i and j. In applying the relations for the equilibrium constants as given in (Reference 28), it is noted that free atom ratios $\text{Ni}^{58}:\text{Ni}^{60}:\text{Ni}^{61}:\text{Ni}^{62}:\text{Ni}^{63}$ are the same as in the natural isotopic abundance of nickel; therefore, the ratios such as $[\text{Ni}_2^{ij}/\text{Ni}_2^{ik}]$ can be determined from the ratios of the equilibrium constants for the individual isotopic reactions.

$$\frac{K}{\sigma_{ij}} = \frac{[\text{Ni}_2^{ij}]}{[\text{Ni}^i][\text{Ni}^j]} \quad (28)$$

$$\frac{\sigma_{ik}}{\sigma_{ij}} = \left(\frac{\text{Ni}_2^{ij}}{\text{Ni}_2^{ik}} \right) \left(\frac{\text{Ni}^i}{\text{Ni}^j} \right) \left(\frac{\text{Ni}^k}{\text{Ni}^i} \right) \quad (29)$$

$$\frac{\sigma_{ik}}{\sigma_{ij}} = \left(\frac{\text{Ni}_2^{ij}}{\text{Ni}_2^{ik}} \right) \left(\frac{\text{Ni}^k}{\text{Ni}^j} \right) \quad (30)$$

For example: in the above equations, letting $i = 60$, and $k = 58$ then if $i = j$ it follows that $i, j = i, i = 60, 60$, while $i, k = 60, 58$; furthermore, $\sigma_{ij} = 2$ and $\sigma_{ik} = 1$ respectively, and the ratio $\text{Ni}^{58}:\text{Ni}^{60} = 67.52:26.32 = 2.565$ and one obtains the following value for the ratio of the diatomic molecules.

$$[\text{Ni}_{60,60}^{60}/\text{Ni}_{58,60}^{58}] = 1/2 [\text{Ni}^{60}/\text{Ni}^{58}] = 1.283 \quad (31)$$

Since the mass spectrometer determines mass numbers, all possible combinations of i and j whose sums are equal to a given mass number contribute to the current for a given mass number and, therefore, must be included in determining the relative ratios of the mass numbers. For example Ni_2^{116} and Ni_2^{118} can be formed only by the combination $\text{Ni}^{58}\text{Ni}^{58}$ and $\text{Ni}^{59}\text{Ni}^{59}$, respectively, while the molecule Ni_2^{120} can be formed from the combination $\text{Ni}^{60}\text{Ni}^{60}$ and $\text{Ni}^{58}\text{Ni}^{62}$.

Computation of the ratios of all possible combinations of isotopes which contribute to abundance Ni_2^{120} , Ni_2^{118} , and Ni_2^{116} , yield the following ratios: $[\text{Ni}_2^{116}:\text{Ni}_2^{118}:\text{Ni}_2^{120}] = 1:0.78:0.257$. The discrepancy of these ratios to those reported by Kant (Reference 42), given above, puts the experimental accuracy of Kant's data under suspicion but because the data

presented is independent of his determination of the molecular isotopic ratios, the dissociation energy $[D_0^\circ(\text{Ni}_2)]$ can still be estimated by using Kant's data, and the relations he used. The relation for D_0° (Equation 32) which was derived by Drowart and Honig (Reference 49), appears to have an error in the constant, therefore, a derivation will be given of Equation 32 so that the value of the constant can be checked by the reader.

Relations for Determining $D_0^\circ(\text{Ni}_2)$ from Spectroscopic Data

Equation 32 is the relation given by Drowart and Honig (Reference 49) for the dissociation energy of a diatomic molecule in terms of spectroscopically derived quantities. In this particular case it is assumed that the diatomic molecule is the dimer of the atom.

$$\begin{aligned} \frac{D_0^\circ}{2.303RT} = & -\log P_1 (\text{mm}) + \log (I_2^+/I_1^+) - \log (\gamma_2/\gamma_1) \\ & + 3/2 \log T + \log M_1 + \log Q_{1el} \\ & - \log Q_{2el} - 2 \log r_2 - \log Q_{2v} + 3.2771 \end{aligned} \quad (32)$$

In Equation 32, P_1 (Torr) is the pressure of the monomer in Torr, (I_2^+/I_1^+) , is the ratio of diatomic current to atomic currents. The diatomic current is of course the sum of the currents of the isotopically different masses which comprise the dimer and the atomic current is the sum of isotopic atomic currents. It is further assumed that $(I_2^+/I_1^+) = [P_2/P_1]$ where P_2 is the pressure of the diatomic molecule. The symbols γ_1 and γ_2 represent the products of ionization cross section and multiplier efficiency for the atom ion and diatomic ion-molecule respectively; T is the temperature in $^\circ\text{K}$; M_1 is the atomic weight of the atom, which in the case of Ni equals 58.7. Q_{2el} and Q_{1el} are electronic partition functions for Ni_2 and Ni, respectively. Q_{2v} is the vibrational partition function for (Ni_2) ; r_2 is the radius of the diatomic molecule, (Ni_2) ; R is the gas constant, and 3.2771 is a constant. The quantities used by Kant (Reference 49) and those used herein to recalculate the values of $D_0^\circ(\text{Ni}_2)$ are given in Table XIII.

TABLE XIII
DATA USED TO CALCULATE D_0° BY EQUATION 32

<u>Term</u>	<u>Expression or Value</u>
$[\gamma_2(\text{Ni}_2)/\gamma_1(\text{Ni})]$	$1^{(a)}$
M_1	$58.71^{(a)}$ g/mole
$Q_{el}(\text{Ni}_2)$	$1^{(b)}$
$Q_{el}(\text{Ni})^{c,d}$	$9 + 7 \exp \left[-\frac{1917}{T} \right] + 5 \exp \left[-\frac{3191}{T} \right]$ $+ 7 \exp \left[-\frac{2948}{T} \right] + 5 \exp \left[-\frac{1267}{T} \right]$ $+ 3 \exp \left[-\frac{2466}{T} \right] + 5 \exp \left[-\frac{4909}{T} \right]$
r	$2.30\text{\AA}^{(a)}$
$Q_v^{(a), (e)}$	$\left[1 - \exp - \frac{467.7}{T} \right]^{-1}$
constant in relation 32	$3.2771; 2.8247^{(a)}$

(a) Value given in Reference 42.

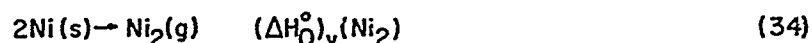
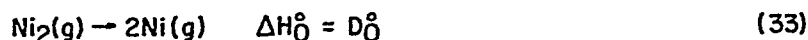
(b) This value of $Q_{el}(\text{Ni}_2) = 1$ is obtained by assuming that the ground state of (Ni_2) is 1Σ . This differs from the assumption in Reference 42. The choice of the 1Σ g.s. is based on the possible electronic configurations of Ni_2 [Reference 37].

(c) Reference 42 has a typographical error in this expression.

(d) The electronic levels (cm^{-1}), and their degeneracies, of the nickel atom which contribute to the partition function are as follows: 0.0(9), 204.8(7), 879.8(5), 1332.2(7), 1713.1(3), 2216.5(5), 3409.9(5).

(e) The vibrational frequency of Ni_2 was assumed to be 325 cm^{-1} . The value was obtained by taking 1.25 x Debye frequency of the solid as in Reference 42.

The equations and numerical constants used in deriving Equation 32 are obtained from the relations given by Herzberg (Reference 50) and the JANAF Tables (Reference 28). The free energy functions which are utilized are those for the species in Reactions 33, 34, and 35.



The changes in free energy functions for these reactions are related to equilibrium constants for the reactions and may be combined as shown in Equation 36 and 37 for Reaction 33.

$$-\Delta\left(\frac{G-H_0^\circ}{RT}\right) = -2\left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}(\text{g})] + \left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}_2(\text{g})] \quad (36)$$

$$-\Delta\left(\frac{G^\circ-H_0^\circ}{RT}\right) = \log [K_p]_{\text{eq } 33} + \frac{D_0^\circ}{RT} = \log \frac{P^2[\text{Ni}]}{P[\text{Ni}_2]} + \frac{D_0^\circ}{RT} \quad (37)$$

In Equation 37 the relations between the change in standard free energy ΔG° , and the equilibrium constant was utilized; as well as the expression for the equilibrium constant in terms of the partial pressures and activities of the species involved.

Rearranging terms and combining Equations 36 and 37 the following equations are obtained:

$$\log [K_p]_{\text{eq } 33} + \frac{D_0^\circ}{RT} = -2\left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}(\text{g})] + \left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}_2(\text{g})] \quad (38)$$

$$\log P(\text{Ni}) + \log \frac{P(\text{Ni})}{P(\text{Ni}_2)} + \frac{D_0^\circ}{RT} = -2\left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}(\text{g})] + \left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}_2(\text{g})] \quad (39)$$

Finally

$$\frac{D_0^\circ}{2.303RT} = -\log P(\text{Ni}) + \log \frac{P(\text{Ni}_2)}{P(\text{Ni})} - 2\left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}(\text{g})] + \left(\frac{G^\circ-H_0^\circ}{RT}\right) [\text{Ni}_2(\text{g})] \quad (40)$$

The quantity $\left[-\frac{G^\circ - H_0^\circ}{T} \right] [\text{Ni(g)}]$ is the free energy function of nickel atom and can be calculated from the sum of the relations for the electronic and translational contributions to the free energy.

The translational contribution to the free energy function is given by

$$-\left(\frac{G^\circ - H_0^\circ}{T}\right)_{\text{trans}} = 6.863753 \log M + 11.439588 \log T - 7.283739 \text{ cal/deg/mole} \quad (41)$$

In the above equation, M is the molecular weight of the species and T is the temperature in $^\circ\text{K}$.

The electronic contribution is given by:

$$-\left(\frac{G^\circ - H_0^\circ}{T}\right)_{\text{el}} = 4.575835 \log \sum_i g_i \exp - \frac{1.438840 \epsilon_i}{T} \text{ cal/deg/mole} \quad (42)$$

where ϵ_i is the energy of the i th electronic level, g_i is the degeneracy of i th level and summation, \sum_i is taken over all electronic levels.

For diatomic molecules the translational and electronic contribution to the free energy function is given by Equations 41 and 42 and vibrational and rotational contributions are given as follows:

$$-\left(\frac{G^\circ - H_0^\circ}{T}\right)_{\text{rot}} = -4.575835 \log \frac{B\sigma}{T} + 0.953116 (B/T) + 0.0457127 (B/T)^2 - 0.723040 \quad (43)$$

In the above expression σ is the symmetry number which is equal to 2 for homonuclear molecules and 1 for heteronuclear molecules. When considering a mixture of isotopes, the symmetry number for diatomic molecules of the same element is equal to 2. However, when the distribution of isotopic mixtures of diatomic molecules of the same element is being determined the molecules have a symmetry of 1 when the molecules are composed of different isotopes and 2 when they are composed of the same isotope (Reference 47).

The rotational constant B is given by the relation

$$B = \frac{2.798890 \times 10^{-39}}{\mu r^2} \quad (44)$$

where r is the radius of the diatomic molecule, μ is the reduced mass which for homonuclear molecules is equal to ($M_1/2$). Where M_1 is the atomic weight of the element. When the value of B is obtained from spectroscopic data it is given by $B = (B_e - \frac{\alpha_e}{2})$ where B_e is the value of B at the equilibrium distance between the atoms, and α_e is a correction to be applied due to change of the moment of inertia with vibrational energy. If it is assumed, as it is in most cases, that the rotator is rigid, then the value of B to be used is B_e . In principle however, B must be determined for each vibrational state, but since the variation of B with vibrational energy is small even for high temperatures, the rigid rotator vibrator approximation is accurate enough for most thermodynamic applications. The vibrational contribution to the free energy function is given by:

$$-\left(\frac{G^\circ - H_0^\circ}{T}\right)_{\text{vib}} = -4.575835 \log [1 - \exp -\mu] \text{ cal / deg / mole} \quad (45)$$

where $\mu = (1.43840 \omega/T)$ and ω is the vibrational frequency in cm^{-1} .

Summing the expressions for each degree of freedom for the individual species one obtains the value of $\Delta \left[\frac{G^\circ - H_0^\circ}{T} \right]$ for the dissociation reaction of a homonuclear diatomic molecule such as Ni_2 . For example, evaluating some of the terms such as:

$$\frac{B\sigma}{T} = \frac{2 \times 2.798890 \times 10^{-39} \times 6.00 \times 10^{23}}{\frac{M_1}{2} \times r^2 \times T \times 10^{-16}} \quad (46)$$

where r is given in Angstroms, Equation 46 reduces to

$$\frac{B\sigma}{T} = \frac{67.845}{M_1 \times r^2 \times T} \quad (47)$$

taking the \log_{10} one obtains:

$$\log \frac{B\sigma}{T} = 1.83152 - \log M_1 - \log r^2 - \log T \quad (48)$$

letting $\sigma = 2$, substituting Equation 48 into Equation 43, adding it to Equation 41, and dividing the result by $2.303R$, Equation 49 is obtained.

$$-\left(\frac{G^\circ - H_0^\circ}{2.3RT}\right)_{\text{rot+trans}} = 1.5 \log M_1 + 2.5 \log T - 3.5803 + \log r^2 - \log T + \log M_1 \quad (49)$$

Summing the electronic vibrational, translational, and rotational contributions to the free energy function, expression 50 is obtained for the free energy function of a homonuclear diatomic molecule.

$$-\left(\frac{G^\circ - H_0^\circ}{2.30RT}\right)_{\text{+vib+elec}}^{\text{(trans+rot)}} = 2.5 \log M_1 + 3.5 \log T + \log r^2 + \log(Q_{el}) - \log Q_v - 3.5803 \quad (50)$$

In Equation 50, Q_v and Q_{el} are the vibrational and electronic partition functions respectively. Combining the above expression with the corresponding expression for the atom the change in the free energy function for the reaction $[Ni_2 \rightarrow 2Ni]$ is obtained by subtracting the free energy function of Ni_2 from twice the free energy function of Ni atoms, which gives the following expression for the change in the free energy function for the dissociation reaction.

$$-\Delta\left(\frac{G^\circ - D_0^\circ}{2.3RT}\right) = 0.5 \log M_1 + 1.5 \log T + \log \frac{Q_{el}^2(Ni)}{Q_{el}(Ni_2)} + \log Q_v(Ni_2) - 2 \log r(Ni_2) + 0.3963 \quad (51)$$

Combining Equation 51 with Equation 40 and expressing the pressure P in Torr one obtains Equation 52.

$$\frac{D_0^\circ}{2.3RT} = -\log P_{\text{Torr}}(Ni) + \log \frac{P(Ni_2)}{P(Ni)} + \log \frac{M_1/2T^{3/2}}{r^2(Ni_2)} + \log \frac{Q_{el}^2(Ni)}{Q_{el}(Ni_2)} + \log Q_v(Ni_2) + 0.3963 + 2.8808 \quad (52)$$

where 2.8808 is the $\log 760$. The conversion to Torr is required since free energy functions were defined with reference to a standard state at one atmosphere.

$$\text{The ratio } \frac{I^+(Ni)}{I^+(Ni_2)} = \frac{P(Ni)Y_2}{P(Ni_2)Y_1} \quad (53)$$

where γ_1 is the product of the ionization cross section and the electron multiplier efficiency for a given species. If it is assumed as was in Reference 42 that $(\gamma_2/\gamma_1) = 1$, then $[I^+(Ni)/I^+(Ni_2)] = P(Ni)/P(Ni_2)$ or Equation 52 becomes Equation 54.

$$\begin{aligned} \frac{D_0^\circ}{2.30RT} = & -\log P_{\text{Totr}}(Ni) + \log \frac{P(Ni_2)}{P(Ni)} + \log \frac{M^{1/2} T^{3/2}}{r^2(Ni_2)} \\ & + \log \frac{Q_{el}^2(Ni)}{Q_{el}(Ni_2)} + \log Q_v(Ni_2) + 3.2771 \end{aligned} \quad (54)$$

Utilizing Equation 54, the free energy functions given by Hultgren (Reference 3), the "best value" of ΔH_{298}° for the vaporization nickel obtained in this report, the data given by Kant for the ratio of the ion currents, and the constants in Table XIII a value of $D_0^\circ(Ni_2) = 61.7 \pm 0.6$ kcal per mole was obtained in contrast to the value reported by Kant (Reference 42) of 53.3 kcal/mole.

APPENDIX II

IONIZATION CROSS SECTIONS USED IN MASS SPECTROMETRIC
VAPOR PRESSURE MEASUREMENTS

Section 1 Examination of Ionization Cross Section Data

In the report of the mass spectrometric measurements of the vapor pressures and enthalpies of vaporization of nickel oxide (NiO)_g, nickel (Ni)_g and oxygen (O_2)_g from nickel oxide solid by Grimley, Burns and Inghram (Reference 4) discussed on p. 32 etc., the values of the ionization cross section of silver and oxygen atoms, and the relative values of the ionization cross sections of silver, nickel, and oxygen atoms, and oxygen molecules were required to obtain the absolute pressures of these species in the system. The values used in Reference 4, were the relative cross sections calculated by Otvos and Stevenson (Reference 51), which are inconsistent with the experimentally determined values of cross sections of silver and oxygen atoms; therefore, it was necessary to re-examine the data in Reference 4, utilizing the best values of cross sections of hydrogen atoms, oxygen atoms, oxygen molecules and silver atoms, and the relative cross sections of silver and nickel atoms. The best values of these cross sections were determined as indicated in the subsequent discussion.

Since many of the calculated and observed ionization cross sections reported in the literature are given relative to that of the hydrogen atom, it was necessary to obtain a "best value" of the cross section for ionization of the hydrogen atom. The best value for this cross section was obtained from a critical analysis of the ionization cross section measurements reported by Kieffer and Dunn (Reference 52). Referring to Figure 6 (Figure 3, Reference 52), it is noted that the two curves representing ionization cross sections as a function of the electron energy are composites of data of equal reliability, presented by four different groups of investigators. The value of the ionization cross section which is of primary interest in the discussion is the maximum value (σ_m). The "best value" of σ_m can be obtained by averaging the voltage for the maximum cross sections, and in turn averaging the cross

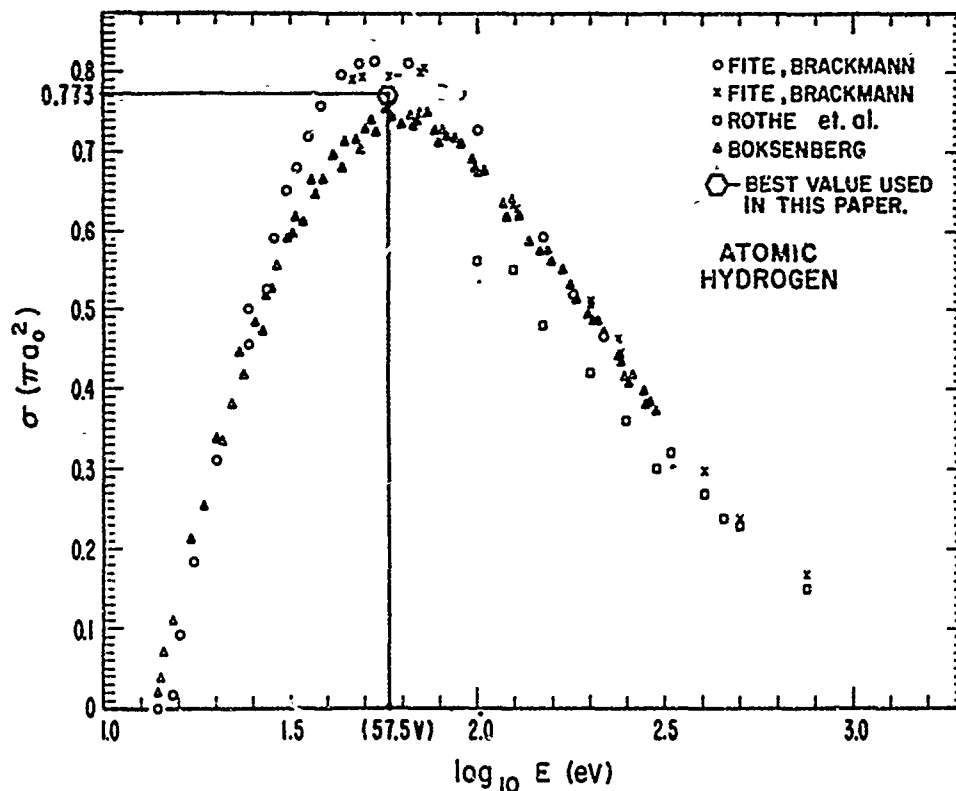


Figure 6. Normalized Cross Sections for Ionization of Atomic Hydrogen. O-Fite, Brackmann are the data referred to by the authors as "relative"; they were normalized to Born approximation calculation at 500 ev. X-Fite, Brackmann are the data referred to by the authors as "absolute"; they were normalized using the total absolute cross sections measured by Tate and Smith (Reference 53) for molecular hydrogen. References: Fite, Rothe, Boksenberg, (References 54, 55 and 56 respectively). [Figure 3, Kiefer and Dunn, Rev. Mod. Phys. 38, 1 (1966)]

sections at these voltages. The averaging process is valid since the curves are flat at the maxima. Upon examination, one curve yielded a value of $\sigma_m = 0.66 \times 10^{-16} \text{ cm}^2$ at 60 volts and the other curve a value of $\sigma_m = 0.70 \times 10^{-16} \text{ cm}^2$ at 53 volts, thus giving an average value of $\sigma_m = 0.68 \times 10^{-16} \text{ cm}^2$ at 57.5 volts as shown in Table XIV of this report.

The cross sections of the oxygen atoms and the oxygen molecule can also be obtained from the data available in Reference 52. An examination of Figure 7 (Figure 6, Reference 57) combined with the discussion on page 26, Reference 52, leads one to consider only the data of References 55, 56, and 58. The reason the data in Reference 57 was not considered was that it was inconsistent with the data of References 55 and 58 which were consistent with each other in spite of the fact that they represent different method of measuring cross sections. The data which was considered gave a value for ionization cross section for O atom: $\sigma_m = 1.56 \times 10^{-16} \text{ cm}^2$ at 87.8 volts. The ionization cross section for the O_2 molecule as a function of energy is given in Figure 7 (Figure 15, Reference 52). Utilizing the discussion on page 27, Reference 52, a value of $\sigma_m = 2.80 \times 10^{-16} \text{ cm}^2$ at 123 volts was obtained for O_2 molecule. The above values of σ_m for O and O_2 are those shown in Table XIV. Although these values are subject to a number of systematic errors, there is no evidence which would lead us to reject these results in favor of any calculated relative values. Therefore, one is led to use these values as the best available ones when measuring pressures by mass spectrometry.

The absolute value of the ionization cross section of the silver atom was measured by Crawford (Reference 63) who obtained the values shown in Table XIV. Although these values disagree with those in Reference 64 wherein the value reported was $\sigma = 2.68 \times 10^{-16} \text{ cm}^2$ at 70 volts, Crawford's value was accepted because of the consistencies found between this value and other relative cross sections by Rovner and Norman (Reference 65). For example, Rovner and Norman noted that if they used their measured value of the relative ionization cross section of the calcium atom to that of the silver atom: $[\sigma(\text{Ca})/\sigma(\text{Ag})] = 0.63$, in combination with absolute value of the ionization cross section of calcium atom $\sigma(\text{Ca}) = 11.8 \times 10^{-16}$

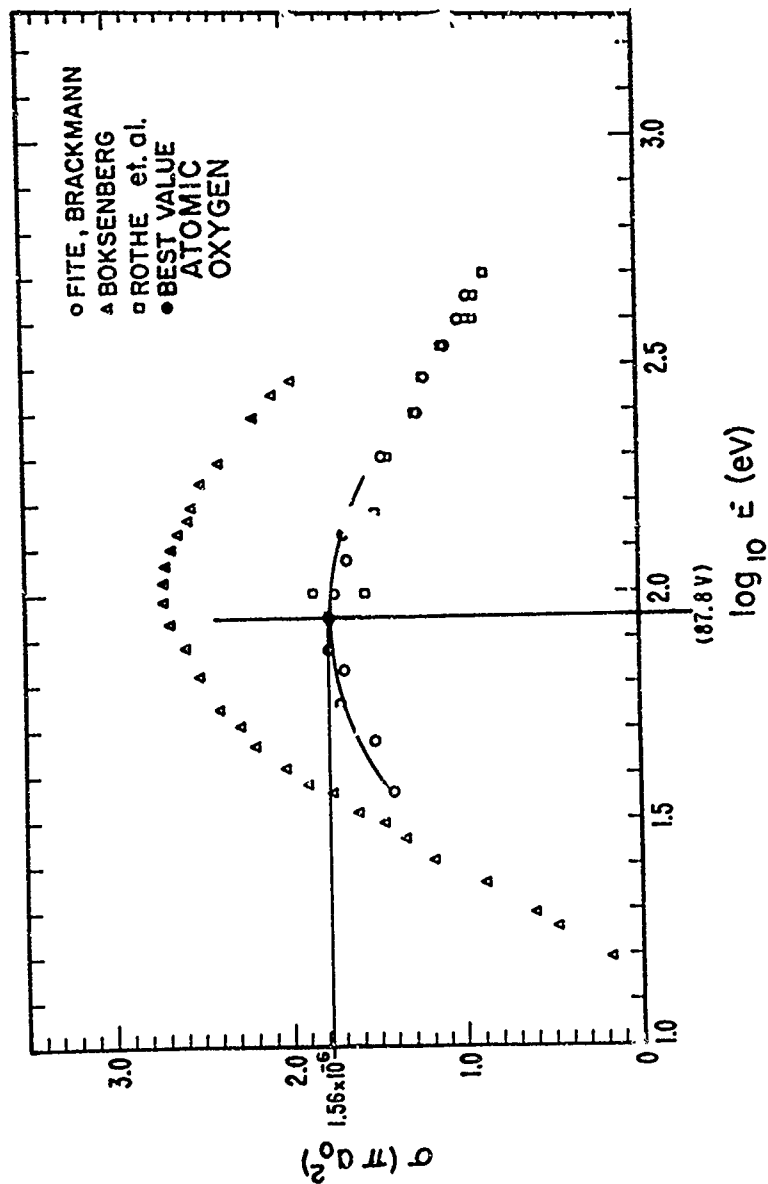


Figure 7. Cross Sections for Ionization of Atomic Oxygen. The data of Rothe (Reference 55) are total cross sections. The data of Fite (Reference 58) and of Boksenberg (Reference 56) because of mass analysis are cross sections for the production of O^+ from O . ($\pi\alpha^2 = 0.88 \times 10^{-16} \text{ cm}^2$) [Figure 17, J. Kieffer and G. H. Dunn, Rev. Mod. Phys. 38, 1 (1966)]

cm^2 obtained by McFarland (Reference 66), they obtained a value for $\sigma(\text{Ag}) = 6.6 \times 10^{-16} \text{ cm}^2$ at 50 volts. Furthermore, Rovner and Norman (Reference 65) noted that using their measured value of the relative cross section of silver atom to lead atom, $[\sigma(\text{Ag})/\sigma(\text{Pb})] = 0.62$, which agrees with the value of $[\sigma(\text{Ag})/\sigma(\text{Pb})] = 0.58$ reported in references 63 and 67, and the absolute value of $\sigma(\text{Pb}) = 8.0 \times 10^{-16} \text{ cm}^2$ (Reference 64), they arrived at a value of $\sigma(\text{Ag}) = 4.8 \times 10^{-16} \text{ cm}^2$ at 50 volts. Thus it was concluded in Reference 65 that the best value of $\sigma(\text{Ag}) = 5.6 \pm 1 \times 10^{-16} \text{ cm}^2$ at 50 V. For the purposes of this report we intend to use the best available measured value for Ag, that is, $\sigma_m(\text{Ag}) = 4.63 \times 10^{-16} \text{ cm}^2$ at 70 volts as shown in Table XIV, since it is consistent with other cross section measurements discussed above.

To obtain a relationship between the measured cross sections and those used in Reference 4, we must discuss the calculation of relative cross sections by Otvos and Stevenson (Reference 51) and indicate the limitation of this calculation in predicting ionization cross sections. Otvos and Stevenson assumed that the maximum ionization cross sections are proportional to the weighted sum of the cross sections of the valence electrons of the atoms. The weighing factor was the relative mean square of the radii of the electrons. They also assumed that the molecular cross sections are the sum of the atomic cross sections. These assumptions are limited by the technique of calculating wave functions of the atoms and also by the fact that no account is taken of the energy of the colliding electron. The effect of the inner shells of the atom on the atomic radii are simply accounted for by correcting the atomic number by a screening constant. The errors thus introduced become accentuated as the atoms become more complex as noted in a comparison between the calculated relative cross sections of sodium, potassium, and hydrogen, and the measured relative cross sections of these atoms. For example, the values of the measured total cross section for sodium atom at its maximum are: $\sigma_m = 6.8 \times 10^{-16} \text{ cm}^2$ (Reference 68); $8.6 \times 10^{-16} \text{ cm}^2$ (References 69 and 70); and $7.6 \times 10^{-16} \text{ cm}^2$ (Reference 71) which upon averaging gives a value of $\sigma_m = 7.7 \times 10^{-16} \text{ cm}^2$, and a relative cross section of sodium with respect to hydrogen (Table XIV); $[\sigma(\text{Na})/\sigma(\text{H})] = 11.3$.

Reference 51 gives a calculated value of $[\sigma(\text{Na})/\sigma(\text{H})] = 14.3$. In contrast a much larger discrepancy between the measured and calculated relative cross section exist for potassium. The measured maximum values of total cross section of potassium at 8.5 volts are $\sigma_m = 7.9 \times 10^{-16} \text{ cm}^2$ (Reference 68), $\sigma_m = 9.6 \times 10^{-16} \text{ cm}^2$ (References 69 and 70) and $\sigma_m = 8.6 \times 10^{-16} \text{ cm}^2$ (Reference 71) yielding an average value of $\sigma_m(\text{K}) = 8.6 \times 10^{-16} \text{ cm}^2$ giving a relative cross section with respect to hydrogen atom of $[\sigma(\text{K})/\sigma(\text{H})] = 12.7$, while the calculated relative cross section $[\sigma(\text{K})/\sigma(\text{H})] = 38.8$ (Reference 51).

Examining the cross section for silver we find similar discrepancies. Utilizing the data in Table XIV it is found that the relative cross section $[\sigma(\text{Ag})/\sigma(\text{H})] = 6.83$ in contrast to the calculated value in Reference 51: $[\sigma(\text{Ag})/\sigma(\text{H})] = 34.8$. Thus there may be considerable error in trying to use the relative cross sections in Reference 51 to obtain absolute values. As a comment on the additivity of cross sections it is noted that measured ratios of $[\sigma(\text{O}_2)/\sigma(\text{O})] = 1.80$, which differs from the value of 2.0 predicted in Reference 51.

Since no measured value of the absolute ionization cross section of the nickel atom is available, the relative value of $[\sigma_m(\text{Ag})/\sigma_m(\text{Ni})]$ reported by Cooper et al (Reference 72) was utilized to estimate the absolute value of $\sigma_m(\text{Ni})$ even though it was difficult to evaluate the experimental techniques utilized by these authors. The value of $[\sigma(\text{Ni})/\sigma(\text{Ag})] = 0.90$ at 50 V has been reported in Reference 72. Due to the fact that ionization potentials for Ni atoms (7.61 V) (Reference 73) are almost equal to that of silver (7.54 V) (Reference 73) it can be assumed that the ratio of ionization cross sections at the maximum are approximately equal to the ratio at 60 V or that $\sigma_m(\text{Ni}) = 4.19 \times 10^{-16} \text{ cm}^2$.

The extrapolation of the ionization cross section as a function of energy is based on the commonly used relationship between the electron energy and the ionization cross section where the energy is less than that at which the cross section is a maximum.

$$\frac{\sigma_V}{\sigma_m} = \frac{V-V_A}{V_m-V_A} \quad (55)$$

In equation 55, V is the potential corresponding to the electron energy, and V_m is the potential at which the ionization cross section is a maximum, while V_A is the appearance potential, or ionization potential for the molecular species in question.

The above data on cross sections can now be applied to correct enthalpy and vapor pressure data reported by Grimley, et al (Reference 4) as noted in Section 2.

Section 2 Mass Spectrometric Measurements of Vapor Pressure

The measurement of vapor pressure by means of the mass spectrometer requires a knowledge of (1) the number of particles of a given molecular weight which enter an ionization chamber, (2) the fraction of particles in the ionization chamber which are ionized, (3) the molecular weight distribution of the resulting ions, (4) the fraction of ions formed in the ionization chamber which are accelerated into the magnetic field (for magnetic mass spectrometers) and which arrive at the detector, (5) the electron current provided by each ion arriving at the detector. The factors are often stated in terms of a geometric or transmission factor which defines the fraction of particles which are transmitted through each region of the mass spectrometer; the ionization cross section which determines the fraction of particles that are ionized to form a given ion; and the sensitivity of the detector that determines the detector current produced per ion arriving at the detector. The relation between the ionization cross sections, vapor pressures, and geometric factors can be obtained as follows. Referring to Figure 8 and letting

I_e = electron current in the ionization chamber

A = area swept out by the electron beam

l = length of electron path in ionization chamber

$\sigma_j(V)$ = cross section for ionization of species j by the electrons of energy V

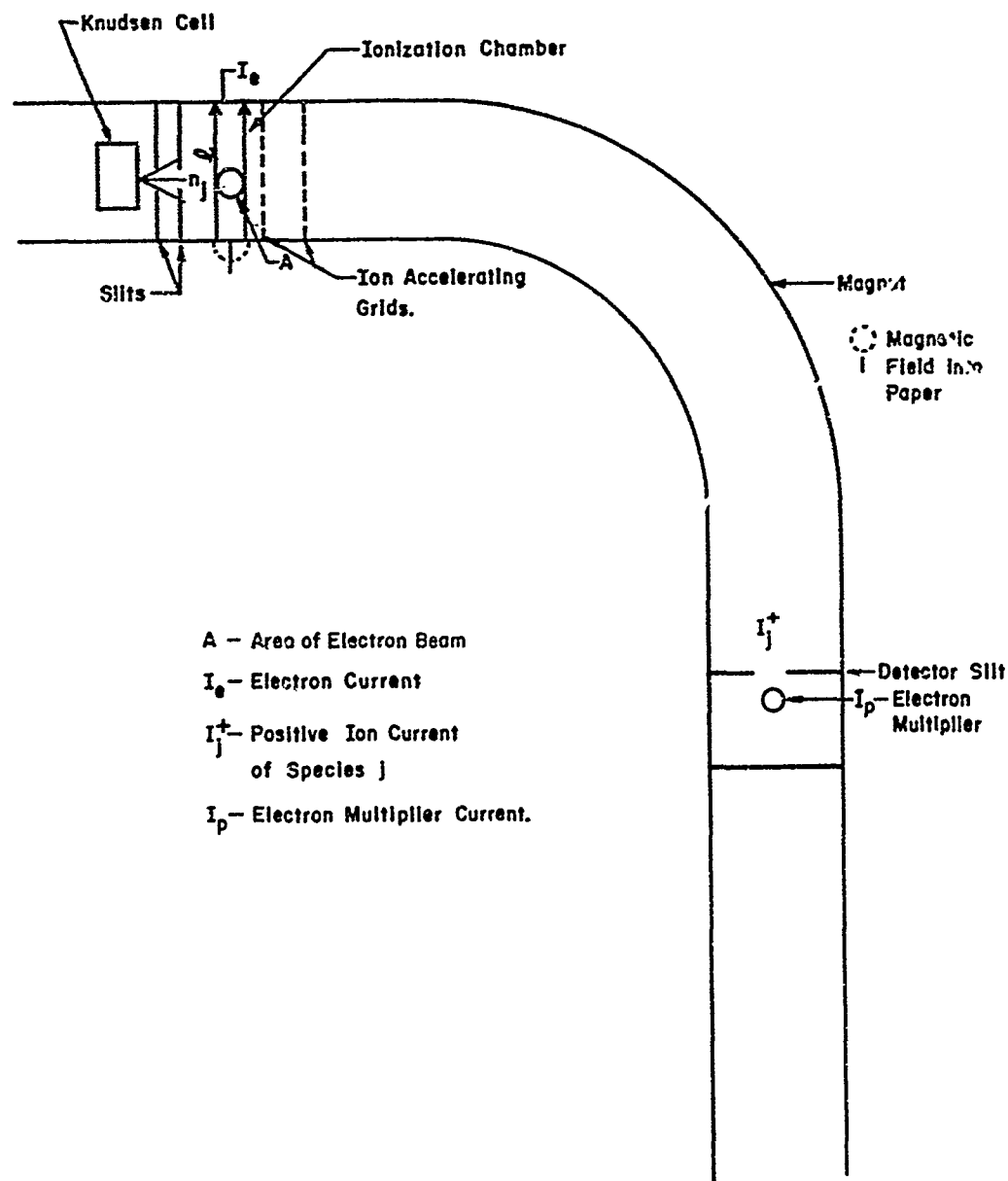


Figure 8. Magnetic Mass Spectrometer Arrangement

$\left(\frac{dn^+}{dt}\right)_j$ = rate of production of positive charge in the ionization chamber due to species j

ρ_j = number density of neutral particles j in the ionization chamber

The following relation holds at constant electron energy between the quantities defined.

$$\left[\frac{dn^+}{dt}\right]_j = \frac{I_e}{A} \sigma_j \rho_j A \ell \quad (56)$$

If the small fraction of the molecules which are ionized can be neglected the density ρ_j in the ionization chamber is obtained from the following relation.

$$\rho_j = \text{flux out of Knudsen cell} \times \text{geometric factor} \times (\text{velocity of particles})^{-1}$$

$$\rho_j = n_j \times G \times v^{-1} \quad (57)$$

The flux out of the Knudsen cell is given by the following relation.

$$n_j = N \times P_j \times (2\pi RT/M_j)^{-1/2} \quad (59)$$

where N is Avagadro's number, P_j is the pressure of jth particle in the cell, M_j molecular weight, T - temperature, R gas constant.

The molecular velocity v in the beam differs from the average velocity in the cell as noted in Equation 60.

$$v = (9\pi RT/8M)^{1/2} \quad (60)$$

The relation between the mass flux from the cell, m_j , and pressure in the cell is given by

$$P_j = m_j (2\pi RT/M_j)^{1/2} \quad (61)$$

while the relation between the n_j and m_j is given by

$$n_j = \frac{Nm_j}{M} \quad (62)$$

which leads to the following expression for ρ_j

$$\rho_j = GNP_j (2\pi RTM)^{-1/2} (9\pi RT/8M)^{-1/2} \quad (63)$$

Rearranging terms we may write

$$G' = G(2\pi M)^{-1/2} (9\pi/8M)^{-1/2} = (2/3\pi)G \quad (64)$$

$$\rho_j = G'NP_j(RT)^{-1} \quad (65)$$

$$\tau \left(\frac{dn_j^+}{dt} \right) = \frac{G'I_e \sigma_j P_j}{k} \quad (66)$$

where k is the Boltzman constant.

To simplify the derivation of the relation between electron multiplier current and positive ion current consider the steady state operation of a continuous electron beam and particle flux. In this case, the rate of production of positive ions (dn_j^+/dt) equals the rate at which ions arrive at the electron multiplier detector divided by a transmission factor (S). The transmission factor accounts for the loss of ions between the chamber and the electron multiplier. The electron multiplier current I_p is proportional to the ion current arriving at the multiplier and is given by Equation 67.

$$I_p = F\tau_j \left(\frac{dn_j^+}{dt} \right) S = F\tau_j I_j^+ \quad (67)$$

F is the electron multiplier amplification factor, and γ_j is the sensitivity of the electron multiplier for the ion j . The sensitivity is primarily a function of molecular weight M_j , for ions of atoms and those of simple molecules of the same energy. If the simple ion fragments at the electron multiplier surface, the sensitivity is then a function of the momentum of the fragments.

Equation 66 can now be rewritten as:

$$I_j^+ T = \frac{I_{pj} T}{F Y_j} = \frac{G' I_e(\sigma_j) P_j}{k} S \ell \quad (68)$$

where k is the Boltzman constant.

Rewriting Equation 68 by taking logarithms to the base e , (\ln), Equation 69 is obtained:

$$\ln I_j^+ T = \ln I_e + \ln \sigma_j + \ln P_j + \ln(G' S \ell / k) \quad (69)$$

or

$$\ln I_j^+ T - \ln \sigma_j = \ln \text{Const} + \ln P_j \quad (70a)$$

$$\ln I_{pj} T - \ln \sigma_j = \ln \text{Const}' + \ln P_j \quad (70b)$$

It is seen from the above relation that errors in the absolute cross section directly affect the value of the (Const) and subsequently all values of the measured pressures which are deduced by using the calibration constants. Since Equation 55 is used to obtain σ , from $[\sigma_{jm}]$ the errors in the use of the maximum cross section given by Otvos and Stevenson (Reference 51) reflect directly on the value of σ_j used in Equations 70a and 70b, and subsequently on the deduced absolute pressures. For example, the value of the cross section of silver which is deduced on the basis on the Otvos and Stevenson calculation is $34.8 \pi a_0^2$ where $\pi a_0^2 = 0.879 \times 10^{-16} \text{ cm}^2$ is the cross section of the H atom or $\sigma_m(\text{Ag}, 70 \text{ ev}) = 30.6 \times 10^{-16} \text{ cm}^2$. The measured value is $\sigma_m(\text{Ag}) = 4.63 \times 10^{-16} \text{ cm}^2$. See Table XIV. The calibration data given in Reference 4 indicates that constant in Equation 70a in error by a factor of $-\ln(30.64/4.63)$. Furthermore the relative cross section of Ni is given in References 4 and 51 as 24.4 which gives an absolute value of $\sigma_m(\text{Ni}) = 21.5 \times 10^{-16} \text{ cm}^2$ in contrast to the value obtained from the combination of several measurements, i.e. $[\sigma_m(\text{Ni})] = 4.19 \times 10^{-16} \text{ cm}^2$. The error in the cross section of nickel atom partially compensates for the error in the (constant) in Equation 70b. For example, the relation between the constants reflecting the use of two different cross sections for silver is given in Equation 71.

$$\ln[(\text{const})_1/(\text{const})_2] = \ln(\sigma_2/\sigma_1)_{\text{Ag}} \quad (71)$$

where const_1 is the constant obtained in Reference 4.

Similarly utilizing the different cross sections for nickel, one obtains from Equation 71 an expression for correcting the data of Reference 4 by the use of the measured cross section. Rewriting Equation 70a to apply to the nickel ion current, Equation 72 is obtained:

$$\ln Tl^+(Ni) - \ln \sigma(Ni) = \ln(\text{const}) + \ln P(Ni) \quad (72)$$

If we designate the vapor pressure measured in Reference 4 as $[P(Ni)]_1$ and the corrected vapor pressure as $[P(Ni)]_2$ Equation 73 is obtained:

$$\ln[\sigma_2(Ni)/\sigma_1(Ni)] = \ln(\text{const}_1/\text{const}_2) + \ln[P_1(Ni)/P_2(Ni)] \quad (73)$$

Substituting $\ln[\sigma_2(\text{Ag})/\sigma_1(\text{Ag})]$ for $\ln[\text{const}_1/(\text{const}_2)]$ from Equation 71, Equation 74 is obtained which leads to a relation between the reported and the corrected vapor pressure, Equation 75.

$$\ln[\sigma_2(Ni)/\sigma_1(Ni)] = \ln[\sigma_2(\text{Ag})/\sigma_1(\text{Ag})] + \ln[P_1(Ni)/P_2(Ni)] \quad (74)$$

$$\ln[\sigma_2(Ni)/\sigma_1(Ni)][\sigma_1(\text{Ag})/\sigma_2(\text{Ag})] = \ln[P_1(Ni)/P_2(Ni)] \quad (75)$$

Utilizing the values for σ_j given in Table XIV the corrected value $P_2(Ni) = 0.78 P_1(Ni)$ is obtained.

Grimley, et al (Reference 4), also reported the vapor pressure of oxygen in equilibrium with NiO. This data was examined in light of the absolute cross section data that is available. They determined the pressure of oxygen from a measurement of the ratio of O^+ ion to the O_2^+ which was assumed to be related by the equilibrium constant, Equation 77 for the following reaction:



$$K_p = \frac{P(O)}{[P(O_2)]^{1/2}} \quad (77)$$

A value for the pressure inside the Knudsen cell can be obtained from the following consideration; assuming that the reaction in the cell is given by Equation 78 and that



the pressure of oxygen in the cell must satisfy the following steady state relationship: [Rate of Vaporization of O_2] = [Rate of Condensation of O_2] - [Rate of Effusion of O_2] - [1/2 Rate of Effusion of O]. (79)

The last term accounts for the loss of O_2 due to the dissociation Reaction 76 and can be related the partial pressure of O atom. If the rate of vaporization is the maximum possible for the temperature of the system then it is equal to the maximum rate of condensation, that is the rate of collision of O_2 molecules with the sample surface at the equilibrium pressure.

The individual rates noted above can be expressed as follows if we assume that the vaporization coefficient and Clausing factors are unity

$$\text{Rate of Vaporization: } \left[\frac{dn(\text{O}_2)}{dt} \right]_v = A [P(\text{O}_2)]_e \left[2\pi k T M(\text{O}_2) / N \right]^{-1/2} \quad (80)$$

$$\text{Rate of Condensation: } \left[\frac{dn(\text{O}_2)}{dt} \right]_{\text{con}} = A [P(\text{O}_2)]_c \left[2\pi k T M(\text{O}_2) / N \right]^{-1/2} \quad (81)$$

$$\text{Rate of Effusion of } \text{O}_2: \left[\frac{dn(\text{O}_2)}{dt} \right]_{\text{eff}} = g [P(\text{O}_2)]_e \left[2\pi k T M(\text{O}_2) / N \right]^{-1/2} \quad (82)$$

$$\text{Rate of Effusion of O: } \left[\frac{dn(\text{O})}{dt} \right]_{\text{eff}} = g [P(\text{O})]_c \left[2\pi k T M(\text{O}) / N \right]^{-1/2} \quad (83)$$

In the above expression A is the cross sectional area of the sample and a is the cross-sectional area of the effusion hole. For any given species the relation between the equilibrium pressure and the pressure in the cell is obtained from the above relations which reduce to

$$A[P(O_2)]_e = A[P(O_2)]_c + a[P(O_2)]_c + 1/2 a[P(O)]_c [M(O_2)/M(O)]^{1/2} \quad (84)$$

The ratio $[M(O_2)/M(O)]^{1/2} = \sqrt{2}$ while the ratio $[P(O)]/[P(O_2)]^{1/2} = K$. Noting that $(a/A) \approx .01$ and the $P(O) \approx .01 P(O_2)$ we may neglect the difference between $[P(O_2)]_c$ and $[P(O_2)]_e$ and further assume that mass flow rates from the cell are equal to those at the equilibrium pressures. These relations allowed Grimley, et al (Reference 4) to use the observed oxygen ion currents to determine the constants in equation 70, by using the ratio of cross sections as noted.

$$\ln [I^+(O)/I^+(O_2)] - \ln [\sigma(O)/\sigma(O_2)] = \ln [P(O)/P(O_2)] \quad (85)$$

$$\left[\frac{I^+(O)}{\sigma(O)} \right] \times \left[\frac{\sigma(O_2)}{I^+(O_2)} \right] = [P(O)/P(O_2)] \quad (86)$$

Substituting the expression for the equilibrium constant for the ratio of the pressures,

$$\left[I^+(O)/I^+(O_2) \right] \left[\sigma(O_2)/\sigma(O) \right] = K [P(O_2)]^{-1/2} \quad (87)$$

The ratio $[\sigma(O)/\sigma(O_2)] = 0.50$ if the cross sections in Reference 51 are used and the $[\sigma(O)/\sigma(O_2)] = 0.56$ if the data in Table XIV is used. The value of the ratio $[P_1(O_2)/P_2(O_2)]$ which is determined by the use of the Otvos and Stevenson (Reference 51) cross sections, in conjunction with the measured cross sections is given by

$$[\sigma_1(O_2)/\sigma_1(O)] / [\sigma_2(O)/\sigma_2(O_2)] = [P_2(O_2)/P_1(O_2)]^{1/2} \quad (88)$$

or that the pressure of oxygen as determined by using the measured instead of the calculated cross section is 1.24 $[P(O_2)]$ as determined by the use of the calculated $(O + S)$ (Reference 51) cross section].

Since the (const_1) in equation 70a assumes that the electron beam current is a constant, no relation between the apparatus (constant) as determined by the oxygen calibration technique vs. the silver calibration can be readily drawn. However, it is noted that under the same experimental conditions the use of the calculated cross sections instead of the measured cross sections introduces a ratio of 3.2 between the factors in the (constant) which are independent of the operating conditions of the instrument.

Since the pressure of $\text{NiO}_{(g)}$ is of interest in determining the heat of vaporization of $\text{NiO}_{(s)}$, the pressures reported by Grimley (Reference 4) must be corrected for the change in cross sections reported in Table XIV. Grimley, et al, reported using a relative cross section 27.7 for NiO which is equal to the sum of the (O+S) cross sections: $\sigma(\text{Ni}) + \sigma(\text{O})$. Due to the lack of more exact information in this report it is assumed that $\sigma(\text{NiO}) = \sigma(\text{Ni}) + \sigma(\text{O})$, but that the value of $\sigma(\text{Ni}) = 4.19 \times 10^{-16} \text{ cm}^2$ and $\sigma(\text{O}) = 1.56 \times 10^{-16} \text{ cm}^2$ or the value $\sigma(\text{NiO}) = 5.75 \times 10^{-16} \text{ cm}^2$. The correction to the pressure of $(\text{NiO})_g$ due to the correction in cross section is given by Equation 75 as applied to NiO where σ_1 is the (O + S) (Reference 51) cross section and σ_2 are the measured cross sections in Table XIV.

$$\left[\frac{\sigma_2(\text{NiO})}{\sigma_1(\text{NiO})} \right] \left[\frac{\sigma_1(\text{Ag})}{\sigma_2(\text{Ag})} \right] = \left[\frac{P_1(\text{NiO})}{P_2(\text{NiO})} \right] \quad (89)$$

Substituting the values of the cross sections from Table XIV into Equation 89 gives $P_2 = 0.641P_1$. This value of P_2 was used to recalculate the heats of vaporization of $\text{NiO}_{(s)}$ as reported in Part II of this report. Corrections were also made to reported pressures of O_2 and the data of Reference 4 was recalculated (Part II of this report). The recalculation indicated that the mass spectrometer is reliable under suitable operating conditions in generating absolute pressures.

TABLE XIV
IONIZATION CROSS SECTIONS

Species	Voltage	$\sigma \times 10^{+16} \text{ cm}^2$	$\sigma_m(0+S)^f$	Exp relative
H	Max 57.5 ^(a)	0.68 ^(a)	1	1
O	Max 87.8 ^(b)	1.56 ^(b)	3.29	2.29
O ₂	Max 123.0 ^(c)	2.80 ^(c)	6.58	4.12
Ag	Max 72 ^(d)	4.63 ^(d)	34.8	6.83
Ag	50	4.48 ^(d)		
Ag	60	4.50 ^(d)		
Ni	60	4.10 ^(e)		
Ni	Max 70	4.19	24.4	

(a) Figure 7 (Reference 52, p. 11, Figure 3).

(b) Figure 8 (Reference 52, p. 12, Figure 6, data of Rothe and Fite).

(c) Reference 52, p. 18, Figure 17. The total ionization cross section was used for these calculations because the electron energy used in mass spectrometric studies may vary from 10 to 70 ev but it is often limited to 20 ev when dissociation is to be avoided. In cases where the electron energy is greater than 20 ev corrections should be made for the dissociation of O₂. Reference 52, p. 43.

(d) Reference 63, Figure 2.

(e) Combination of data References 63, 65, 67, and 72.

(f) Reference 51.

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SUMMARY

The Langmuir technique for determining vapor pressures was utilized to determine the vapor pressure of nickel between 1233 and 1683°K. The vapor pressure data thus obtained was combined with other available data in the literature to obtain a best value for the heat of vaporization of nickel solid and liquid between the temperatures 1233°K and 1895°K. Equations for the vapor pressure of nickel in these temperature ranges were also determined.

The data in the literature used to determine heats of dissociation of the NiO and Ni₂ gaseous molecules was corrected, and revised heats of dissociation of Ni₂ and NiO gaseous molecules were obtained, as well as estimates for heat of vaporization of NiO solid.

The literature on ionization cross sections useful in mass spectrometry was examined, and best values of the ionization cross sections of silver, lead, and nickel were determined.